

A REPORT
FOR THE CONSTRUCTION OF A FACILITY TO INTRODUCE
AND REMOVE BROMOETHANE FROM A FUMIGATION
CHAMBER

Phase I: Fundamental Studies for the Determination of
Design and Operating Parameters

by

Jeff McInerney

and

Marcus Goddard

January 1989

University of New Brunswick
Department of Chemical Engineering
P.O. Box 4400
Fredericton, NB
E3B 5A3

Approved
W. Cole
Gary Harker

TABLE OF CONTENTS

	<u>Page</u>
List of Tables.....	i
List of Figures.....	ii
SUMMARY.....	1
SECTION	
I INTRODUCTION.....	3
II THEORETICAL ANALYSIS	
2.2 Adsorption Equilibria.....	6
2.2.1 Fundamental Aspects.....	6
2.2.2 Equilibrium Isotherms Using a Chromatographic Method.....	7
III EXPERIMENTAL APPARATI	
3.1 Absorption With Reaction Experimental System.....	10
3.2 Adsorption Systems.....	13
3.2.1 Preliminary Studies.....	13
3.2.2 Bench Scale Adsorption Test.....	15
IV EXPERIMENTAL PROCEDURE	
4.1 Absorption With Reaction.....	18
4.2 Adsorption Systems.....	19
4.2.1 Screening of Adsorbents.....	19
4.2.2 Detailed Study of Air-Water System...	20
4.2.3 Bench Scale Adsorption Test.....	20
V RESULTS AND DISCUSSION	
5.1 Absorption With Reaction.....	22
5.2 Adsorption Systems.....	26
5.2.1 Screening Studies.....	26
5.2.2 Regeneration of YAO.....	35
5.2.3 Bench Scale Experiments.....	36
VI CONCLUSIONS.....	46
VII RECOMMENDATIONS.....	47
7.1 Introduction.....	47
7.2 Pilot Plant Facility.....	47
APPENDIX I: Physical Properties of Adsorbents.....	52
APPENDIX II: Details of Pilot Plant Equipment.....	59

LIST OF TABLES

1. Characteristics of the Absorption/Reaction System
2. Physical Properties of Hellex Tower Packing
3. Characteristics of the Bench Scale Adsorption Apparatus
4. Summary of Adsorbent Screening Studies
5. Summary of Regeneration Techniques for YAO
6. Summary of Small Scale Adsorption Tests
7. Pilot Plant Materials and Costs
8. Basis for Pilot Plant Calculations

LIST OF FIGURES

1. A schematic diagram of the absorption with reaction system for bromoethane removal.
2. A schematic diagram of the apparatus used for the preliminary adsorption screening studies.
3. A schematic representation of the apparatus used for the bench scale adsorption experiments.
4. Absorption of bromoethane in water as a function of time using the absorption/reaction apparatus.
5. Absorption of bromoethane using a 1:1 mole ratio of NH_4OH to bromoethane as a function of time.
6. Absorption of bromoethane using a 10:1 mole ratio of NH_4OH to bromoethane as a function of time.
7. Adsorption equilibria for bromoethane on YAO, HTO and XAD-4 adsorbents at 33°C.
8. Adsorptions of bromoethane in the "as received" sample of YAO and after regeneration.
9. A comparison of the adsorption equilibria for bromoethane on YAO at 33°C and 50°C.
10. A comparison of the adsorption equilibria for bromoethane from a mixture of B/E-hellum and B/E-air on YAO at 33°C.
11. Breakthrough curves of bromoethane from three mixtures of bromoethane-hellum, bromoethane-air-water and bromoethane-air.
12. Adsorption equilibrium isotherms for bromoethane on YAO at 23°C determined using the small bench scale apparatus and at 33°C determined using the screening studies apparatus.
13. Bromoethane concentration in the chamber of the bench scale apparatus as a function of time using an initial concentration of 2.2 mol% bromoethane in air.
14. Bromoethane concentration in the chamber of the bench scale apparatus as a function of time using an initial concentration of 5.3 mol% bromoethane in air.
15. Bromoethane concentration in the chamber of the bench scale apparatus as a function of time using an initial concentration of 4.0 mol% bromoethane in air.

16. Bromoethane concentration in the chamber of the bench scale apparatus as a function of time using an initial concentration of 2.78 mol% bromoethane in air.
17. Bromoethane concentration in the chamber of the bench scale apparatus as a function of time using an initial concentration of 5.8 mol% bromoethane in air.
18. Bromoethane concentration in the chamber of the bench scale apparatus as a function of time using an initial concentration of 3.81 mol% bromoethane in air.
19. A schematic diagram of an adsorption pilot plant for handling bromoethane.

SUMMARY

Agriculture Canada and the New Brunswick seed potato industry have an annual requirement to break dormancy on seed potato samples prior to post harvest testing in Florida. The current facility which is used to accomplish chemically induced dormancy release has been determined to be inadequate resulting in very poor growth and emergence of the sample tubers in Florida. The results of this test procedure are required in order to sell any seed lots to the state of Maine.

Bromoethane has been shown to effectively break the dormancy period of seed potatoes but an economic and environmentally safe technology for application and removal of bromoethane from a leak-tight chamber is required. We report here the results of a study to evaluate an adsorption system for capture and releasing bromoethane from a suitable porous adsorbent. Preliminary analysis of another method which would react bromoethane with an aqueous ammonium hydroxide solution in an absorption column to produce compounds that would be easily disposed was shown to be an ineffective technology.

Adsorbents were selected from four possible candidates, three were carbon-based and one a synthetic resin. Single component adsorption isotherms for bromoethane at 33°C were determined chromatographically using each of the four possibilities. The synthetic resin as well as one of the carbon based adsorbent (a carbon molecular sieve) were shown to have a low adsorption capacity for bromoethane and are

therefore unsuitable. Two activated carbons, YAO and HTO had similar adsorption capacities for bromoethane but the more economic YAO eliminated the HTO as a possible adsorbent.

More detailed studies of the YAO activated carbon revealed that bromoethane may be conveniently removed from the adsorbent by gentle heating (less than 150°C) with vacuum. The adsorption capacity is reduced only slightly when bromoethane is adsorbed from air saturated with water, but the rate of adsorption is reduced when water is present.

Based on the results of these investigations, the cost and design of a pilot plant facility for treating potato tubers is recommended. This facility would be able to process up to 100 kg of bromoethane vapour in air (saturated with water) from a 10,000 ft³ exposure chamber.

I INTRODUCTION

Seed potatoes require a lengthy period of time between harvesting and replanting if new plants are to grow. This dormancy requirement affects the seed potato industry in a number of ways. Firstly, some post-harvest testing procedures require field grown plants derived from tubers that have had their dormancy broken. This procedure should not interfere with the detection of diseased material. Secondly, the development of new tuber varieties in a greenhouse production system is limited by the dormancy and what is required is a consistent dormancy breaking method to maximize turn-around time. Thirdly, North American seed potato producers are unable to sell to growers in tropical and sub-tropical regions because an insufficient period of dormancy has lapsed between our harvest and the time at which their planting takes place. [By breaking the dormancy period, North American producers would be able to take advantage of these markets.]

Recent work [1-5] indicates that bromoethane is a suitable chemical to break the dormancy of seed potatoes. It has a clear advantage over currently used compounds because of its low toxicity and absence of mutagenic or carcinogenic properties. If bromoethane is to be used routinely for breaking seed potato dormancy on a large scale, what is required is a leak-tight exposure chamber with facilities for bromoethane application and removal.

Two methods are available for handling bromoethane vapour in an acceptable manner after seed potatoes have been treated. One technique is to capture bromoethane in a porous solid adsorbent (an adsorption system). This would allow temporary storage of bromoethane in the adsorbent before being released for a subsequent treatment. The procedure has several advantages; a. the cycling of adsorption following by desorption can be repeated several times, b. a new charge of bromoethane is unnecessary and so handling of a hazardous chemical is minimized.

Another possible method would be to react bromoethane with suitable reactants to chemically convert bromoethane to products that can be easily disposed. One such absorption/reaction system uses aqueous ammonium hydroxide (NH_4OH) with bromoethane to produce ammonium bromide and ethanol. The advantage of this system is that ammonium bromide and ethanol are less hazardous than bromoethane and are relatively easy to handle.

The objective of this study was to examine these two procedures (the adsorption system and the absorption/reaction system) for treating bromoethane and to suggest a preliminary design for a handling technology for processing up to 100 kg of bromoethane vapour in air saturated with water from a $10,000 \text{ ft}^3$ exposure chamber based on the results of the investigation.

References

1. Coleman, W.K. "An Evaluation of Bromoethane for Breaking Tuber Dormancy in Solanum Tuberosum", L. Am Potato J. 60, 161-167 (1983).
2. Coleman, W.K. "Large Scale Application of Bromoethane for Breaking Potato Tuber Dormancy". Am Potato J. 51, 587-589 (1984).
3. Coleman, W.K. and S.E. Coleman "The Effects of Bromoethane and Ethanol on Potato (Solanum Tuberosum) Tuber Sprouting and Subsequent Yield Responses". Am Potato J. 63, 373-377 (1986).
4. Coleman, W.K. "Dormancy Release in Potato Tubers: A Review". Am Potato J. 64, 57-68 (1987).
5. McDonald, J.G. and W.K. Coleman. "Detection of Potato Viruses Y and S in Tubers by ELIZA after Breaking of Dormancy with Bromoethane or Rindite". Am Potato J. 61, 619-622 (1984).

II THEORETICAL ANALYSIS

2.2 Adsorption Equilibria

2.2.1 Fundamental Aspects

When a vapour is allowed to come to equilibrium with a solid surface, the concentration of the compound is always found to be greater on the surface than in the free gas. This is the basis of an adsorption system for removing an adsorbable compound (a sorbate) using a porous solid adsorbent.

For a component of a mixture, at a fixed temperature, the adsorbed phase concentration of that component is a function of the partial pressure in the gas phase. Experimentally we can determine the adsorbed phase concentration as a function of partial pressure of that component - the resulting plot is the adsorption equilibrium isotherm. Isotherms show two distinct regions; at low concentrations, the amount adsorbed is directly proportional to the partial pressure:

$$q = Kp$$

q is the adsorbed phase concentration of a component

p is the partial pressure of the component in the gas phase

K is an equilibrium constant

and at high concentrations, there is a region where the amount adsorbed is not a strong function of the partial pressure. For very high partial pressures, the amount adsorbed reaches a maximum called the saturation limit.

Heat is liberated when adsorption occurs and this amount of heat is called the heat of adsorption. Knowing the equilibrium constant as a function of temperature, the heat of adsorption can be calculated using the following equation:

$$K = K_o \exp (-\Delta H/RT)$$

K is the equilibrium constant
 T is the absolute temperature
 K_o is the pre-exponential constant
 R is the Universal Gas Constant (cal/gmol.°K),
 °K = Kelvin
 ΔH is the heat of adsorption

The strength of the sorbate/adsorbent interaction is quantified by the heat of adsorption - for large values, the energy required to remove the adsorbed compound from the adsorbent is also large.

2.2.2 Equilibrium Isotherms Using a Chromatographic Method

Adsorption equilibrium isotherms can be determined using gravimetric or volumetric studies. For sorbates where there is a high heat of adsorption and that are adsorbed quickly, a constant temperature may be difficult to maintain using these methods and this may influence the equilibrium data. A chromatographic technique is a practical alternative to these more conventional techniques since the intrusion of heat transfer resistances are essentially eliminated.

In a chromatographic experiment, an adsorption column is subjected to a perturbation in the sorbate concentration of the inlet stream and the response of the outlet

concentration is monitored. This response plotted as a function of time is the breakthrough curve. The perturbation can either be a pulse or a step input in concentration - the same information can be obtained from either and in this study a step was used.

For a symmetrical breakthrough curve, the mean residence time t_B , is equal to the mid-point time, i.e.

$$t_B = t, C/C_0 = 0.5$$

C_B is the outlet sorbate concentration at time t

C_0 is the initial concentration at the inlet

For each breakthrough curve we can obtain the effective equilibrium constant, K according to:

$$K = m \left[\frac{t_B}{L/V} - 1 \right]$$

$m = \epsilon/1-\epsilon$, the void volume per unit solid volume
in the bed

L = length of the bed

V = interstitial velocity in the bed,

= $\frac{\text{volumetric flow}}{A \cdot \epsilon}$, A is cross sectional area
of the bed

The effective equilibrium constant is the sum of the equilibrium constants for the helium gas carrier and the adsorbable component:

$$K = K_1 X_1 + K_2 X_2$$

K_1 is the helium equilibrium constant

K_2 is the sorbate equilibrium constant

X_1 is the mole fraction of helium

X_2 is the mol fraction of the sorbate

The amount of carrier gas (in most cases, helium) adsorbed is generally considered to be negligible compared to the sorbate concentration, i.e. $K_1 \gg K_2$. For binary

systems, as $X_1 \rightarrow 0$ and $X_2 \rightarrow 1$ (helium is component 1), the above equation is true and for strongly adsorbed species as $X_1 \rightarrow 1$ and $X_2 \rightarrow 0$, the equation will also hold true.

III EXPERIMENTAL APPARATUS

3.1. Absorption With Reaction System

The purpose of this experimental system was to chemically convert bromoethane vapour using aqueous ammonium hydroxide to produce ammonium bromide and ethanol. A schematic representation of the apparatus is presented in Figure 1 and characteristics of the system are summarised in Table 1.

Liquid is pumped to the top of a packed tower and vapour, entering at the base of the tower, flows counter-currently over a polypropylene packing. Details of the physical properties of the packing are presented in Table 2. The large surface area of the packing provides intimate contacting of the vapour and liquid stream promoting absorption and reaction.

After passing through the tower, vapour is directed to a holding chamber similar in size to the packed tower. Products of the reaction and the unreacted bromoethane remaining in the vapour phase are removed by further recycling through the packed tower. The recycling process continues until the concentration of bromoethane is reduced to acceptable levels (< 200 ppm bromoethane).

Continuous recycling of the aqueous phase is also possible. Liquid from the base of the tower is returned to a surge tank. Another pump can raise the liquid to the top of the tower where it is again brought in contact with bromoethane vapour.

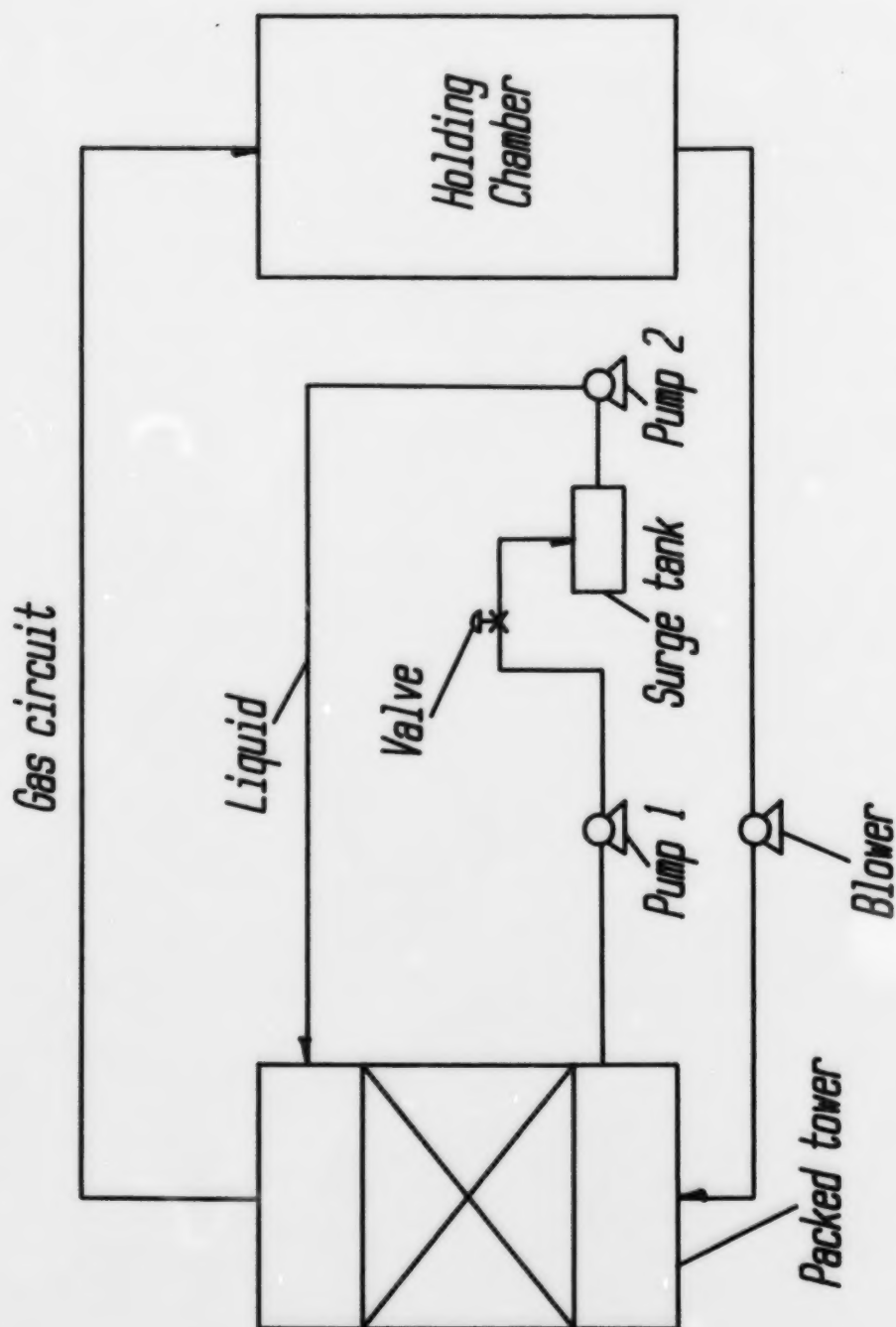


Figure 1: A schematic diagram of the absorption with reaction system for bromoethane removal.

Table 1: Characteristics of the Absorption/Reaction System

Packed Tower Dimension:	0.457 m x 0.457 m x 1.55 m
Height of Packing:	0.634 m
Surge Tank Dimensions:	0.805 m x 0.457 m x 0.406 m
Holding Chamber Dimensions:	0.457 m x 0.457 m x 1.55 m
Gas Flow Rate:	1839 litres/min
Liquid Flow Rate:	2.77 litres/min

Table 2: Physical Properties of Hellex Tower Packing

Size: 2" nominal
Material: polypropylene
Approximate Weight: 4 lbs/ft ³
Approximate Surface Area: 30 ft ² /ft ³
Approximate Number of Pieces: 212/ft ³
% Voidage: 93%
Temperature Limit: 225°F

3.2 Adsorption System

3.2.1 Preliminary Studies

The apparatus employed in preliminary screening and detailed studies of adsorbents is shown schematically in Figure 2. The apparatus consisted of two sections. The first facilitated generation of air or helium gas streams with controlled bromoethane and water vapour contents. The second section was comprised of a packed column containing the adsorbent under study and the gas detection system. Using air as the carrier gas, the gas generation system functioned as follows.

Streams of compressed air were passed through gas wash bottles containing bromoethane and water, respectively. The temperature of the bottles was controlled by two Haake N3 constant temperature baths. The pressure of the inlet gas and the temperature fixed the bromoethane and water vapour concentration in the outlet streams. The rate of gas flow in the combined outlet streams from this section was controlled by two Matheson model 8200 mass flow controllers.

Gas entering the second section passed through a packed bed fabricated from $\frac{1}{2}$ " O.D. copper tubing with $\frac{1}{8}$ " to $\frac{1}{4}$ " Swagelok union fittings used as end caps. A Varian 3400 gas chromatograph equipped with a thermal conductivity detector was used to maintain the temperature of the packed column and measure gas concentrations in the outlet stream. The response of the detector was monitored with a Varian 4290 Integrator.

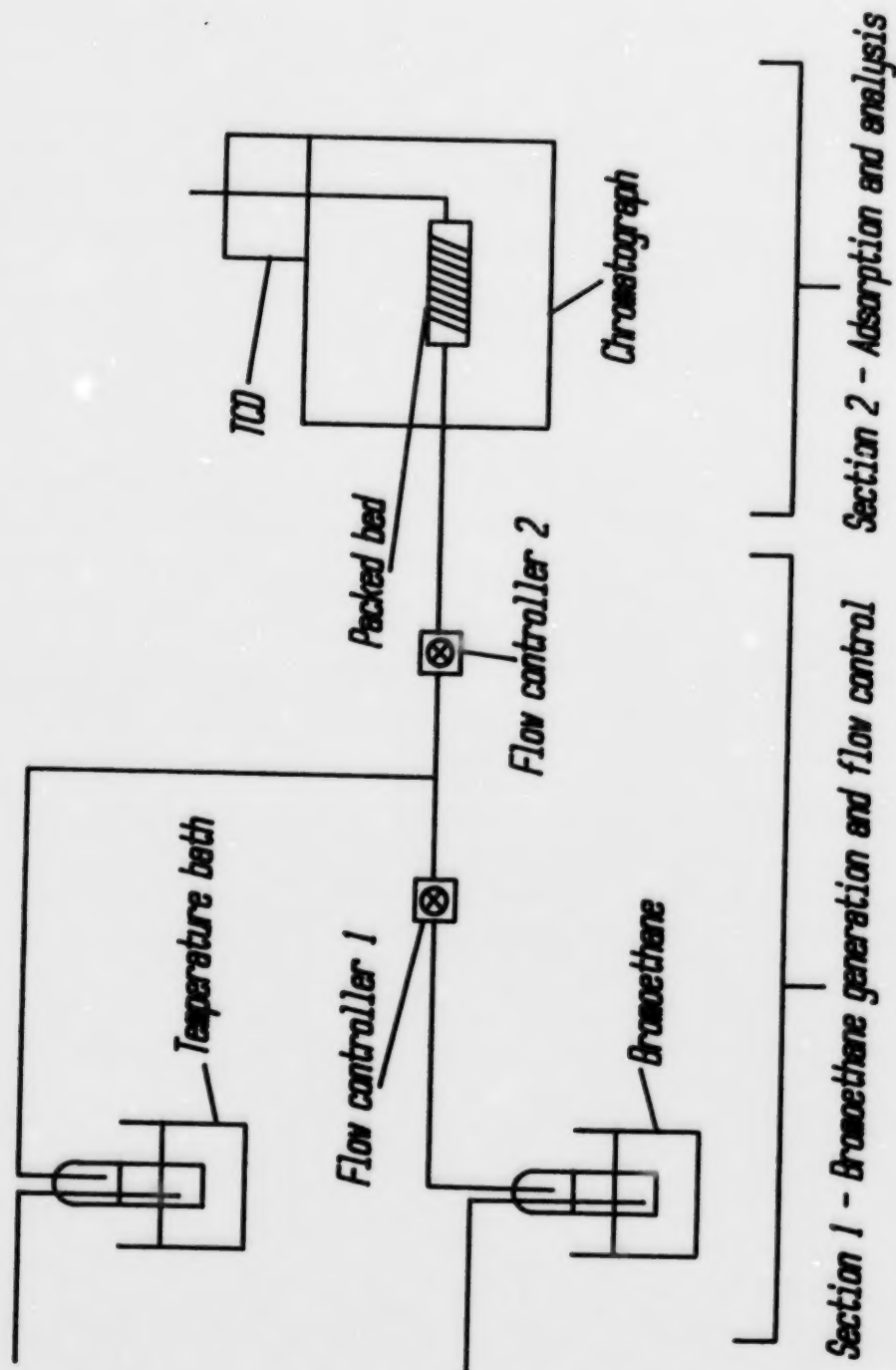


Figure 2: A schematic diagram of the apparatus used for the preliminary adsorption screening studies.

3.2.2 Bench Scale Adsorption Test

The apparatus used in bench scale adsorption studies on YAO granules is shown schematically in Figure 3. The apparatus consisted of an air tight cabinet to which bromoethane could be added and subsequently removed in adsorption. An attached blower recycled the air in the cabinet through the adsorbent bed. During experiments gas samples were removed periodically from the cabinet with a syringe and analyzed by separation on a Haysep column in the Varian 3400 gas chromatograph. Characteristics of the bench scale adsorption setup are given in Table 3.

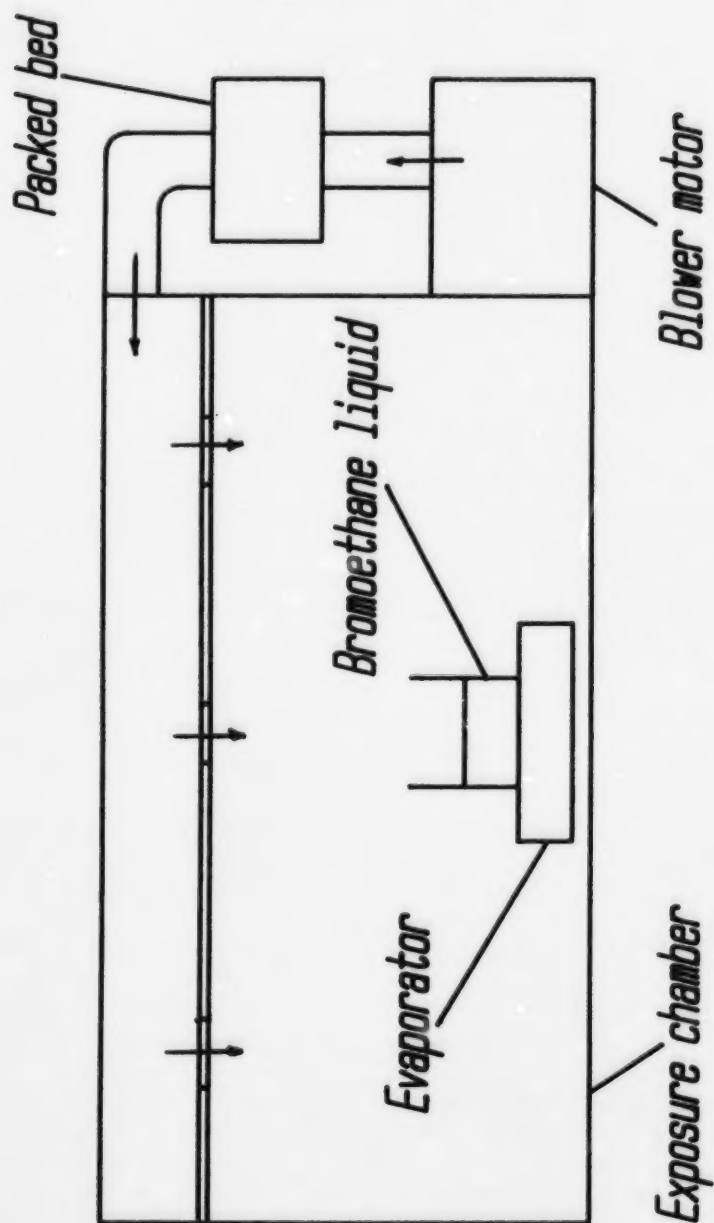


Figure 3: A schematic representation of the apparatus used for the bench scale adsorption experiments.

Table 3: Characteristics of the Bench Scale Adsorption Apparatus

Chamber Volume	295 liters	
Blower Flowrate	164 liters/min	5.79 CFM
Adsorbent	YAO	
Size	4x8 MESH	
Quantity	260 grams	
Bed Diameter	135 mm	
Bed Depth	32 mm	
Face Velocity	1.44 meters/sec	

IV EXPERIMENTAL PROCEDURES

4.1 Absorption With Reaction

The objective of these experiments was to quantify the rate of reaction of bromoethane in air with different initial concentrations of aqueous ammonium hydroxide. Although the initial concentration of bromoethane in air may be higher in a facility for exposing seed potatoes, the goal of this system is to reduce the concentration of bromoethane to an acceptably safe limit. Therefore, the emphasis here was to study the system at initial concentrations of bromoethane lower than those proposed for a large scale treatment facility.

An experimental run began by setting the flow rate of air at its maximum. Liquid flow was adjusted to return to the surge tank at a steady-state rate by a gate valve downstream of pump 1 (see Figure 1). Once this had been achieved, a quantity of liquid bromoethane was injected into the holding chamber; evaporation was almost immediate.

Samples of vapour at five minute intervals (approximately) were withdrawn from the holding chamber using a gas-tight syringe and analyzed by gas chromatography for air, water and bromoethane. Samples were no longer drawn from the holding chamber when the concentration of bromoethane fell below the detection limit of the chromatograph (0.01 mol%).

4.2 Adsorption Systems

4.2.1 Screening of Absorbents

A total of four adsorbents were screened for adsorption of bromoethane from helium. They were:

1. BOC - a carbon molecular sieve
2. Amberlite XAD4 - a polystyrene polymer (Rohme and Haas)
3. HTO - a high capacity activated carbon (Carbon and Filtration Canada)
4. YAO - a medium capacity activated carbon (Carbon and Filtration Canada).

The adsorbents were crushed and sieved to produce a 40-60 mesh material. Each adsorbent was tested in the "as received" condition and after regeneration with helium at 150°C. In the screening test a concentration step chromatographic technique [1] was employed. A given weight of adsorbent was used to fill the packed bed (volume approximately 8 cc). The packed bed was placed in the chromatograph oven, connected to the gas generation section, then maintained at 33°C. The bromoethane generator was held at a pressure of 40 psia and a temperature of 23°C in order to produce a stream of helium containing 22.1 mole percent bromoethane. In this set of experiments water vapor was not added to the helium dilution stream. The mass flow controller on the outlet of the gas generation section was set to 150 cc/min (air). The concentration of bromoethane in helium was increased in a stepwise fashion by varying the setpoint on the other mass flow controller, i.e. by decreasing the helium dilution factor. Because of uptake of

bromoethane by the adsorbent no immediate response to the stepchange was typically detected with the chromatograph. The response of the detector was monitored until a complete breakthrough curve was achieved. The step increases in concentration were repeated until a bromoethane concentration of approximately 6.0 mole percent was reached. The chromatographic response curves were analyzed to obtain retention times and equilibrium concentrations. The packed bed was weighed and the total amount of bromoethane adsorbed determined. The packed bed was regenerated by reverse flow helium purge at 150°C for four hours. Three other regeneration techniques included helium purge at 33°C, vacuum and vacuum desorption plus heat were also tried.

4.2.2 Detailed Studies (Air-Water)

The chromatographic technique was repeated with the YAO activated carbon to determine the adsorption of bromoethane in air-bromoethane and air-water-bromoethane systems. In air-water-bromoethane tests moisture content of the gas stream was maintained at 40 to 50% relative humidity.

4.2.3 Bench Scale Adsorption Test of YAO

A measured quantity of bromoethane was weighed out in a 250 ml beaker. The beaker was placed on a preheated surface within the gas containment chamber. After the bromoethane had completely evaporated an initial gas sample of 0.25 millilitres was taken with a gas-tight syringe. The blower

motor was started causing air in the chamber to circulate through the packed bed. Analysis of a gas sample for bromoethane, water and air with the chromatograph required approximately six minutes. This allowed sampling of gas in the chamber at only six to eight minute intervals. Sampling was continued until equilibrium was achieved between the adsorbent bed and the air in the chamber. At the end of the test the adsorbent was removed from the bed and weighed in order to determine the uptake of bromoethane. Used adsorbent was regenerated by vacuum plus heating to 150°C.

The quantity of bromoethane added to the chamber was designed to produce initial bromoethane concentrations from two to six mole percent. With the 260 g quantity of 4x8 mesh YAO adsorbent this translated into a possible maximum uptake of 45% by the packed bed.

References

1. Kumar, R., "Binary Mixtures of Gases on Zeolites: A Study of Sorption and Kinetic Behaviour By Chromatography", Ph.D. Thesis, University of New Brunswick (1978).

V RESULTS AND DISCUSSION

5.1 Adsorption With Reaction

A preliminary set of three experiments was conducted to test a small scale absorption/reaction system provided by Agriculture Canada. The following liquids were used in the absorption of a concentration of bromoethane produced by evaporating 20 mls of the alkyl halide in the apparatus.

1. Water
2. An aqueous solution of NH_4OH prepared so that a mole ratio of bromoethane to NH_4OH was 1:1.
3. NH_4OH in water to produce a 10:1 mole ratio of NH_4OH to bromoethane.

Presented in Figures 4 to 6 is the concentration of bromoethane in the vapour (mole %) as a function of time. The plots indicate that the rate at which bromoethane is absorbed in water is similar to that of solutions where reaction with ammonium hydroxide occurs. After approximately 80 minutes, the concentration falls below the detection limit of 0.01 mol%. These results suggest, that more concentrated solutions of ammonium hydroxide would be required to reduce the high concentration of bromoethane present in a large scale facility for seed potatoes.

At high concentrations of ammonium hydroxide, the resulting concentration of NH_3 vapour would also be high and a procedure for removing this would also have to be developed. The effect of NH_3 on seed potato growth was unknown and it was for these reasons that this method for handling bromoethane was not pursued.

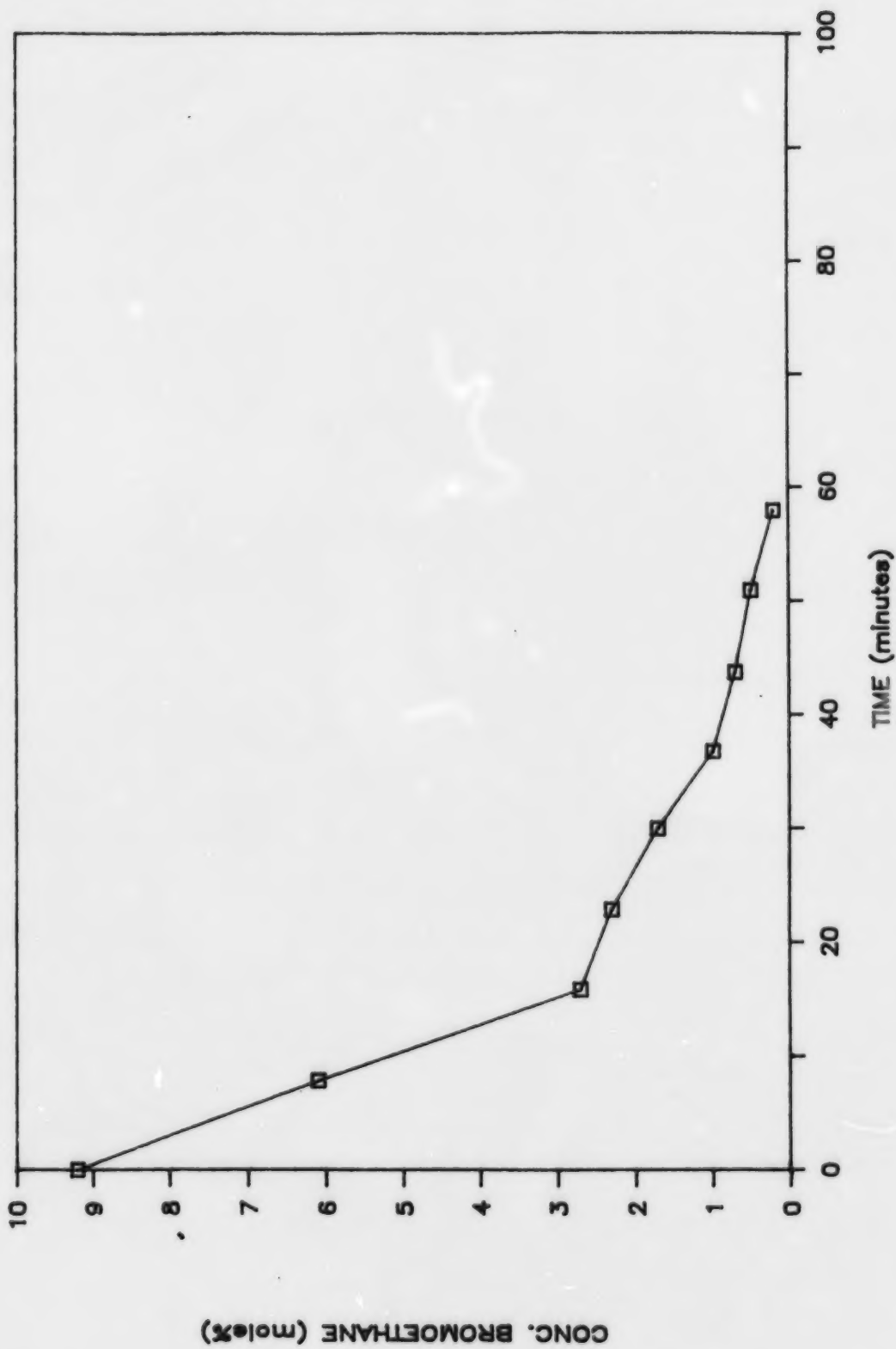


Figure 4: Absorption of bromoethane in water as a function of time using the absorption/reaction apparatus.

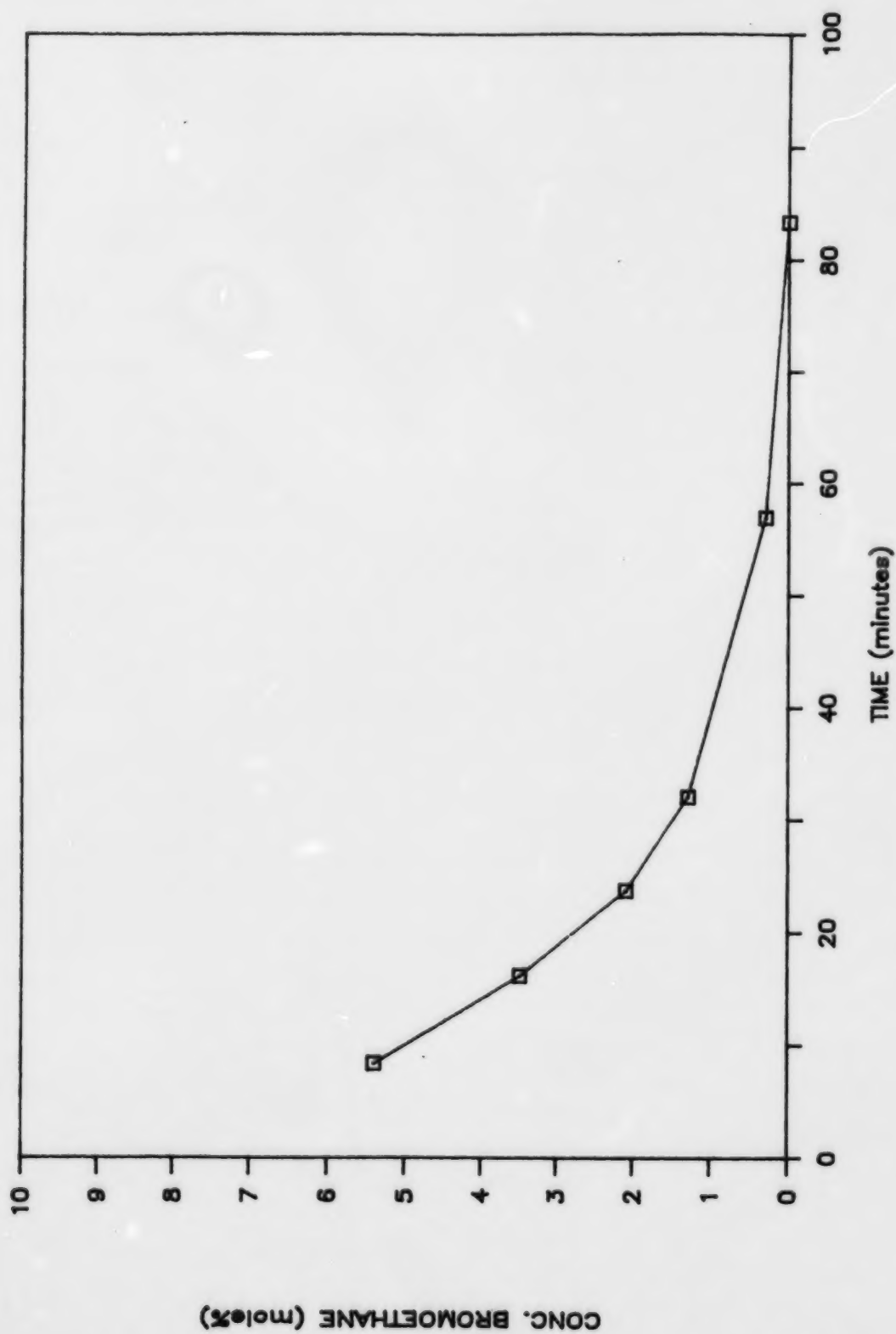


Figure 5: Absorption of bromoethane using a 1:1 mole ratio of NH_4OH to bromoethane as a function of time.

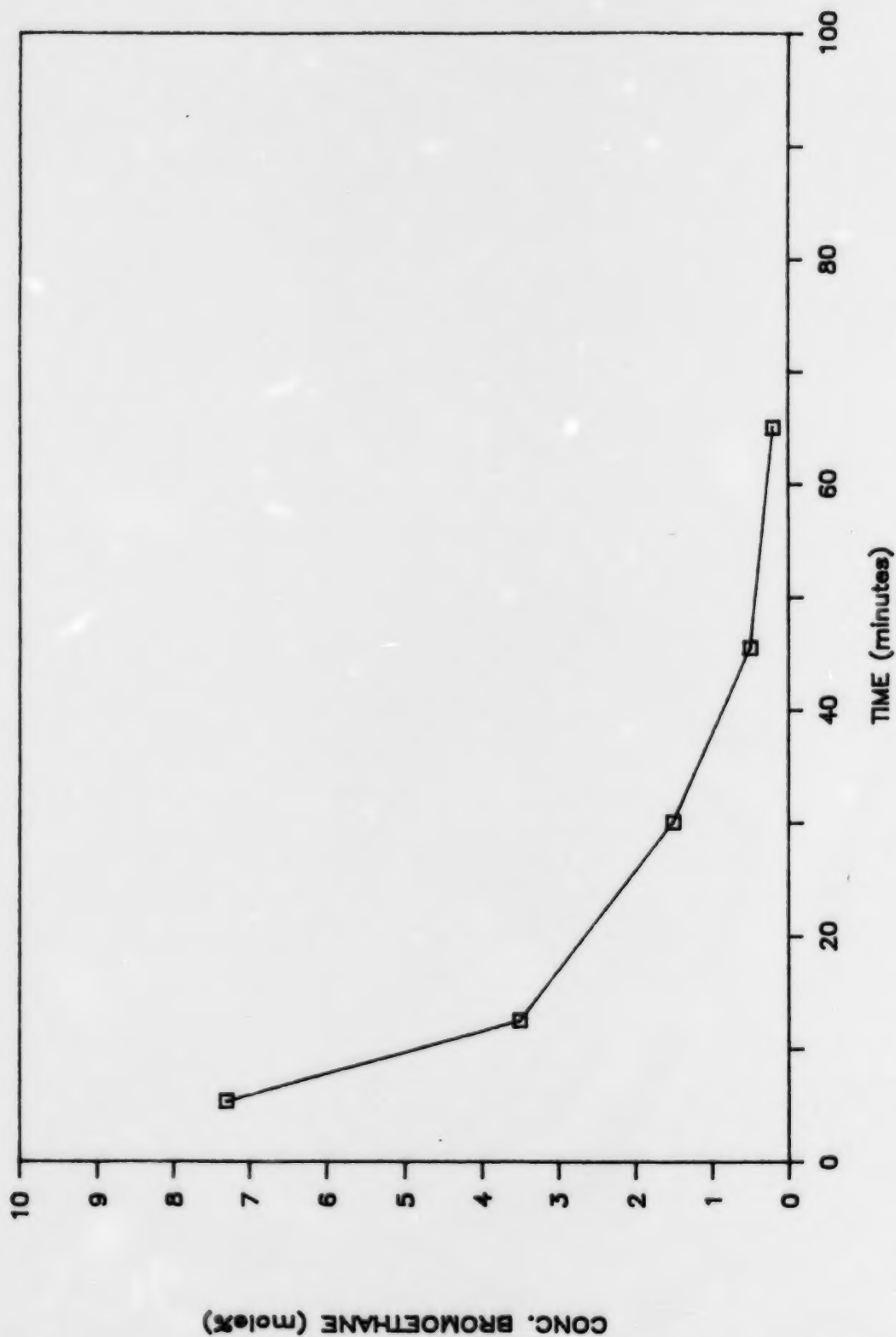


Figure 6: Absorption of bromoethane using a 10:1 mole ratio of NH_4OH to bromoethane as a function of time.

5.2 Adsorption Studies

5.2.1 Screening Studies

The objective of the screening studies was to obtain an adsorbent that would:

- a. have a high adsorption capacity for bromoethane and a low affinity for water adsorption
- b. adsorb bromoethane quickly
- c. easily desorb bromoethane

Pure component adsorption equilibrium isotherms over a wide range of concentrations extending to near saturation at a partial pressure of 0.062 atm were determined chromatographically for a number of possible adsorbents. A summary of the results of these experiments is presented in Table 4 and details of the physical properties of the adsorbents can be found in APPENDIX I.

Table 4: Summary of Adsorbent Screening Studies

Adsorbent	Type	Avg. Particle Size Tested (μm)	Pore Diameter Average ($\text{\AA}$)	Typical Cost (\$/kg)	Wt% Bromoethane adsorbed at 33°C at 0.062 atm
BOC	carbon	442	2.5	10	< 1
YAO	carbon	507	3.20	3.5	59.34
HTO	carbon	475	3.20	7.0	59.32
XAD4	polystyrene	580	40.60	15	17.40

The carbon-molecular sieve was the first of the three carbon-based adsorbents studied. Only small molecules can be admitted into the structure of this adsorbent due to the small size of the pores. Results of the adsorption equilibria indicated that less than 1 wt% was adsorbed at 33°C suggesting that bromoethane could not penetrate the pores of the adsorbent. Clearly, an adsorbent with a wider pore size would be required to achieve a large bromoethane capacity.

Another adsorbent which showed a small capacity for bromoethane was a synthetic resin, XAD-4. At 33°C the maximum capacity after regenerating the sample at 150°C was 17.4 wt% bromoethane. The high cost coupled with the low capacity and a high affinity for water would make this an unsuitable candidate for an adsorption system (see Figure 7).

Equilibrium isotherms for two activated carbon samples YAO and HTO were determined for samples as they were received from the manufacturer and after regeneration at 150°C. Figure 8 shows that for YAO the capacity for bromoethane is higher throughout the range of partial pressures used in these experiments. The difference in adsorbed phase concentration is likely due to water present on the adsorbent when they are received. By regenerating the samples at 150°C the water is removed and a higher capacity for bromoethane is achieved. Figure 7 shows little difference in adsorption equilibrium of the high surface area HTO when compared with YAO suggesting that either

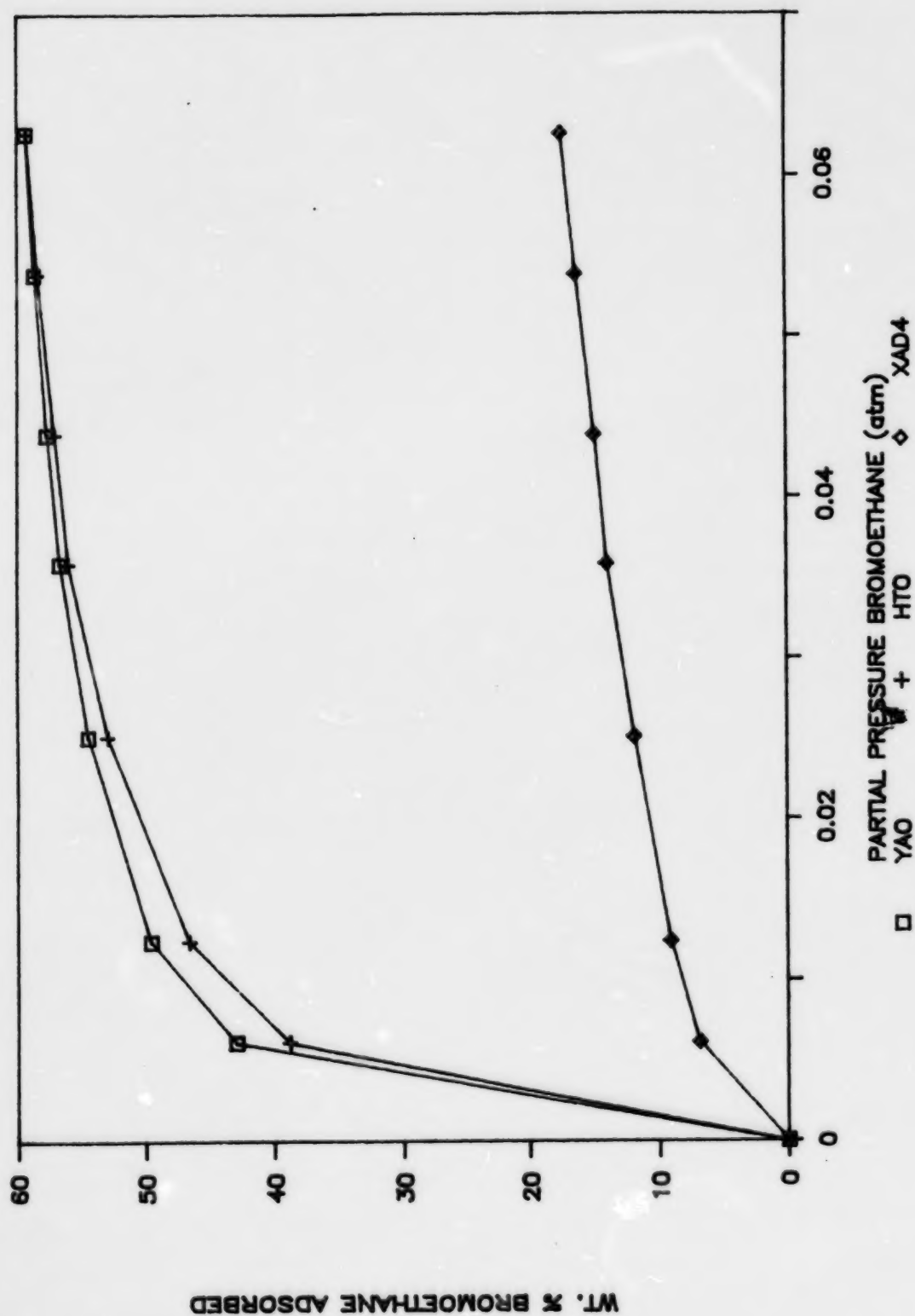


Figure 7: Adsorption equilibria for bromoethane on YAO, HTO and XAD-4 adsorbents at 33°C.

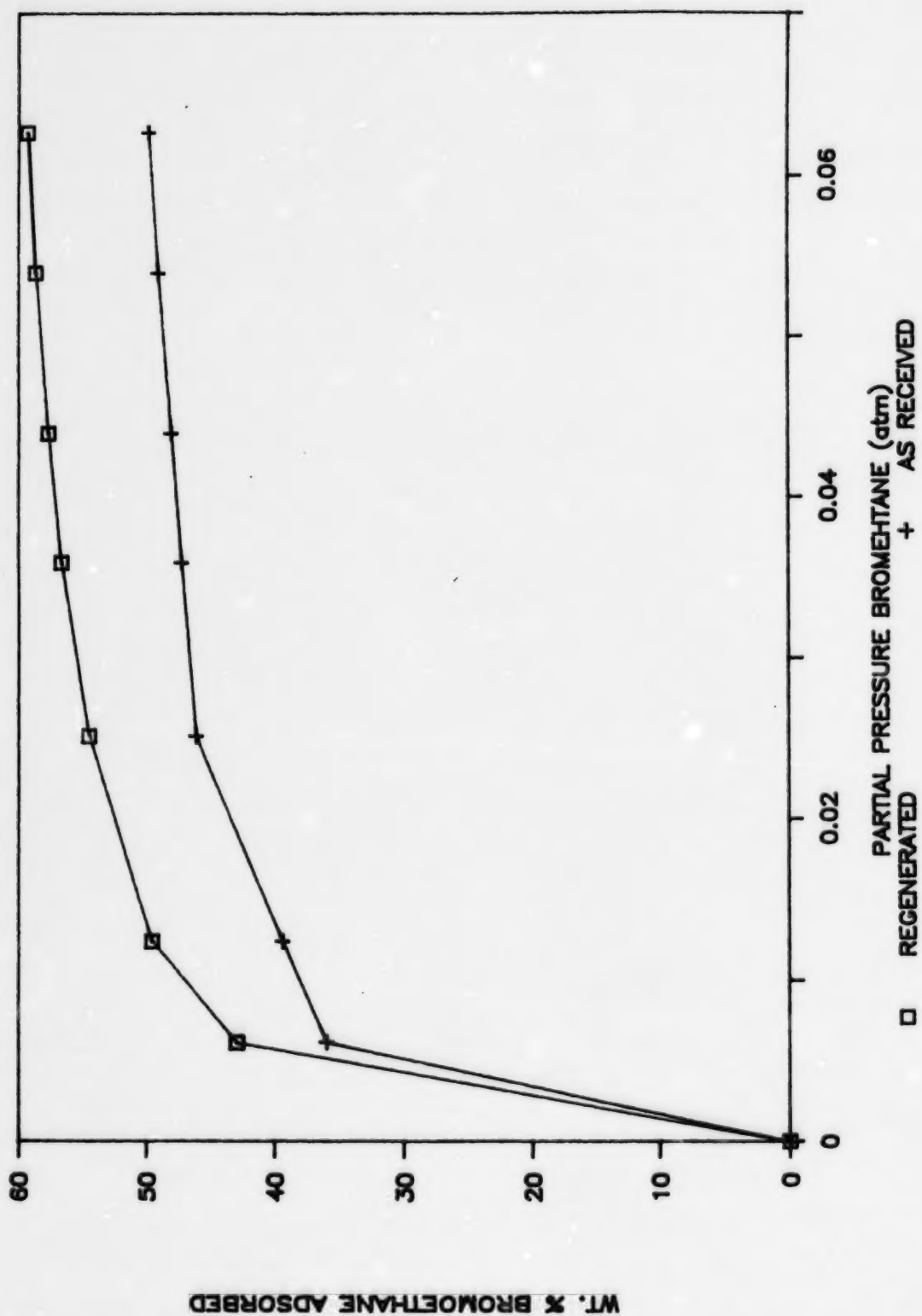


Figure 8: Adsorption of bromoethane on the "as received" sample of YAO and after regeneration.

would be suitable adsorbents but due to the higher cost of the HTO this was eliminated as a possible adsorbent and further studies on the economically attractive YAO were conducted.

The adsorption of bromoethane on YAO was also determined at 50°C in order to estimate the heat of adsorption. In the limiting case, when the concentration of bromoethane approaches 0, the heat of adsorption is approximately 5.4 kcal/mol indicating that bromoethane is only weakly held by the adsorbent at low concentrations. The practical implications of this value for the heat of adsorption is that heating ($\leq 150^{\circ}\text{C}$) or mild heating with vacuum will remove the bromoethane from the adsorbent. Figure 9 shows both the adsorption equilibria determined at 33°C and at 50°C.

For the pure component adsorption isotherms helium was used as a non-adsorbing carrier gas but in a facility for exposing seed potatoes, bromoethane would be recovered from a mixture of air, bromoethane, water and compounds released by the seed potatoes. A series of experiments were conducted to determine how the bromoethane concentration on YAO would be affected with air as a carrier gas and water present in the mixture. Adsorption isotherms presented in Figure 10 showed only a slight decrease in the adsorptive capacity for bromoethane when air, compared with helium is used as a carrier gas. The introduction of water in the mixture reduced the capacity from 57 wt% to 56 wt% for bromoethane.

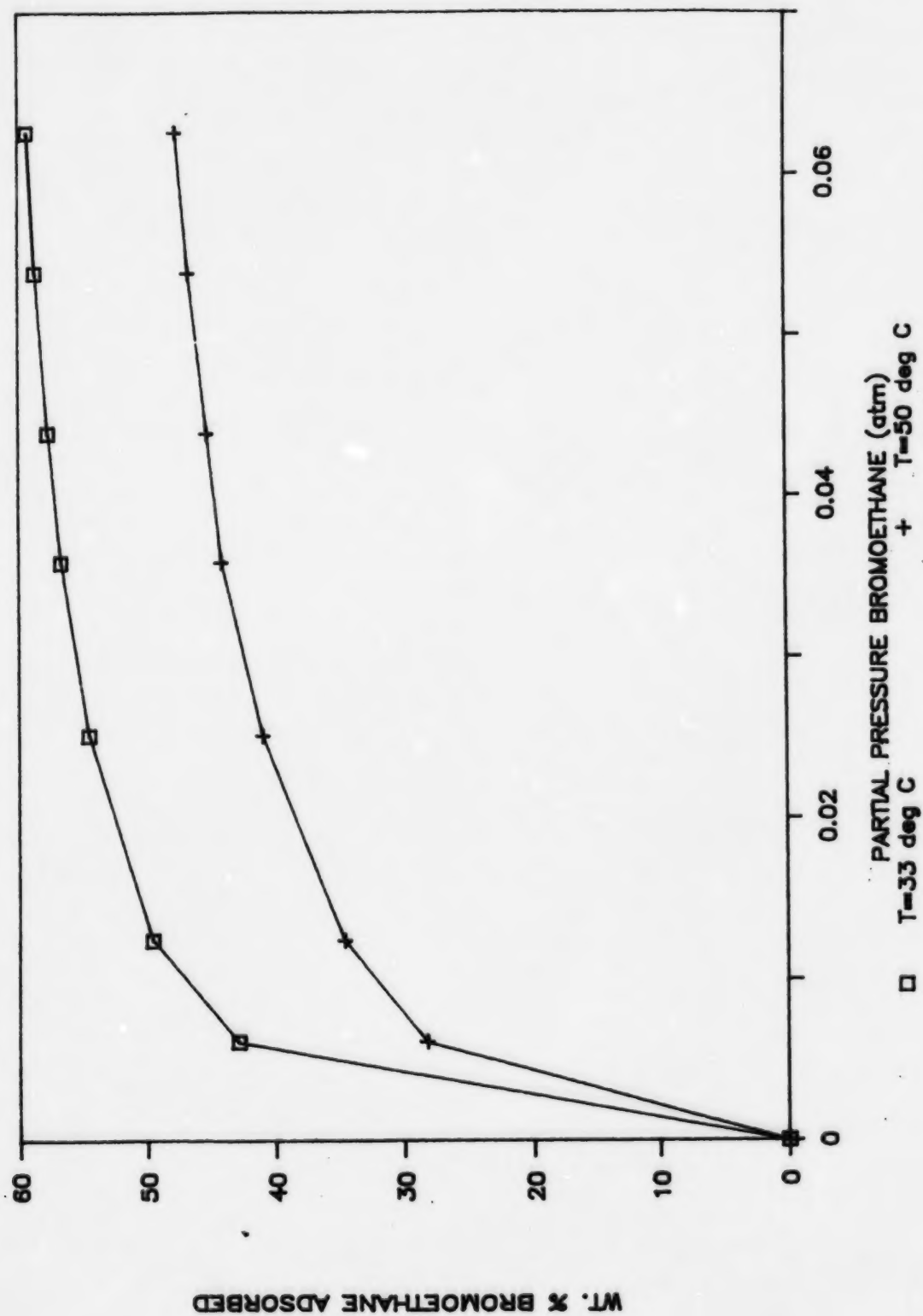


Figure 9: A comparison of the adsorption equilibria for bromoethane on YAO at 33°C and 50°C.

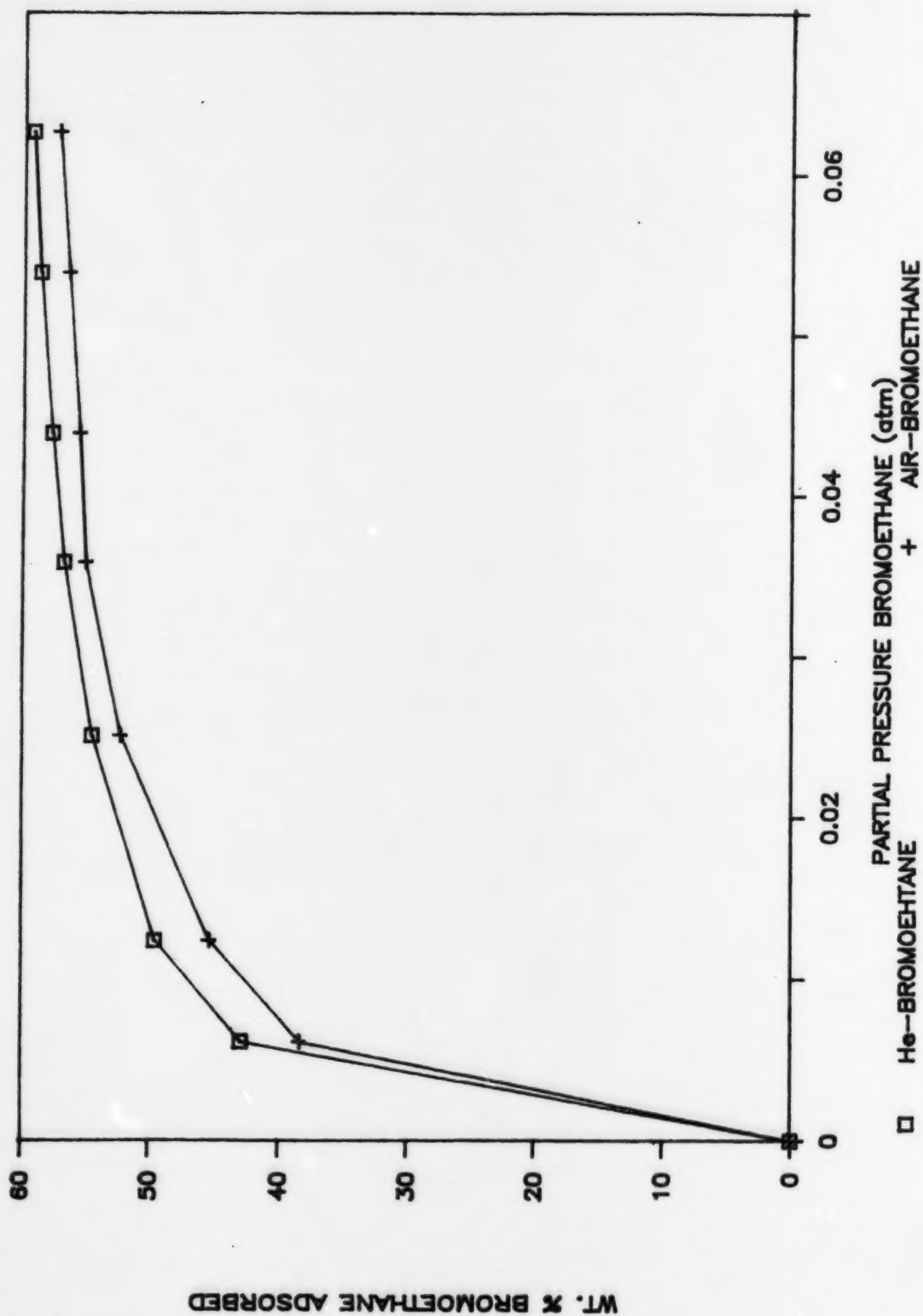


Figure 10: A comparison of the adsorption equilibria for bromoethane from a mixture of B/E-helium and B/E-air on YAO at 33°C.

Shown in Figure 11 are breakthrough curves of bromoethane as a function of time using helium and air as carrier gases as well as an experiment in which water vapour was present at 40-50% relative humidity. The breakthrough curve for the experiment using the helium carrier is delayed compared with the curves for air and air + water. Bromoethane in the air and air-water experiments does not have sufficient time to adsorb onto the surface of the activated carbon and will easily pass through the adsorption column (i.e. it has an early breakthrough). For the experiments using helium, bromoethane adsorption occurs quickly and so the breakthrough is delayed. It should be noted that although the detector response for the air and air-water breakthrough curves are not normalized (the attenuation settings were different for each experiment) the curves indicate similar early breakthrough of bromoethane.

To summarize, these data suggest that even at high concentrations of water, YAO activated carbon does not have a strong affinity for water and the capacity for bromoethane is maintained at the values measured in the absence of water. Analysis of the breakthrough curves indicate that a longer period of time (i.e. a longer residence time) is required in order for equilibrium to be achieved when bromoethane is adsorbed from air or a mixture with water vapour.

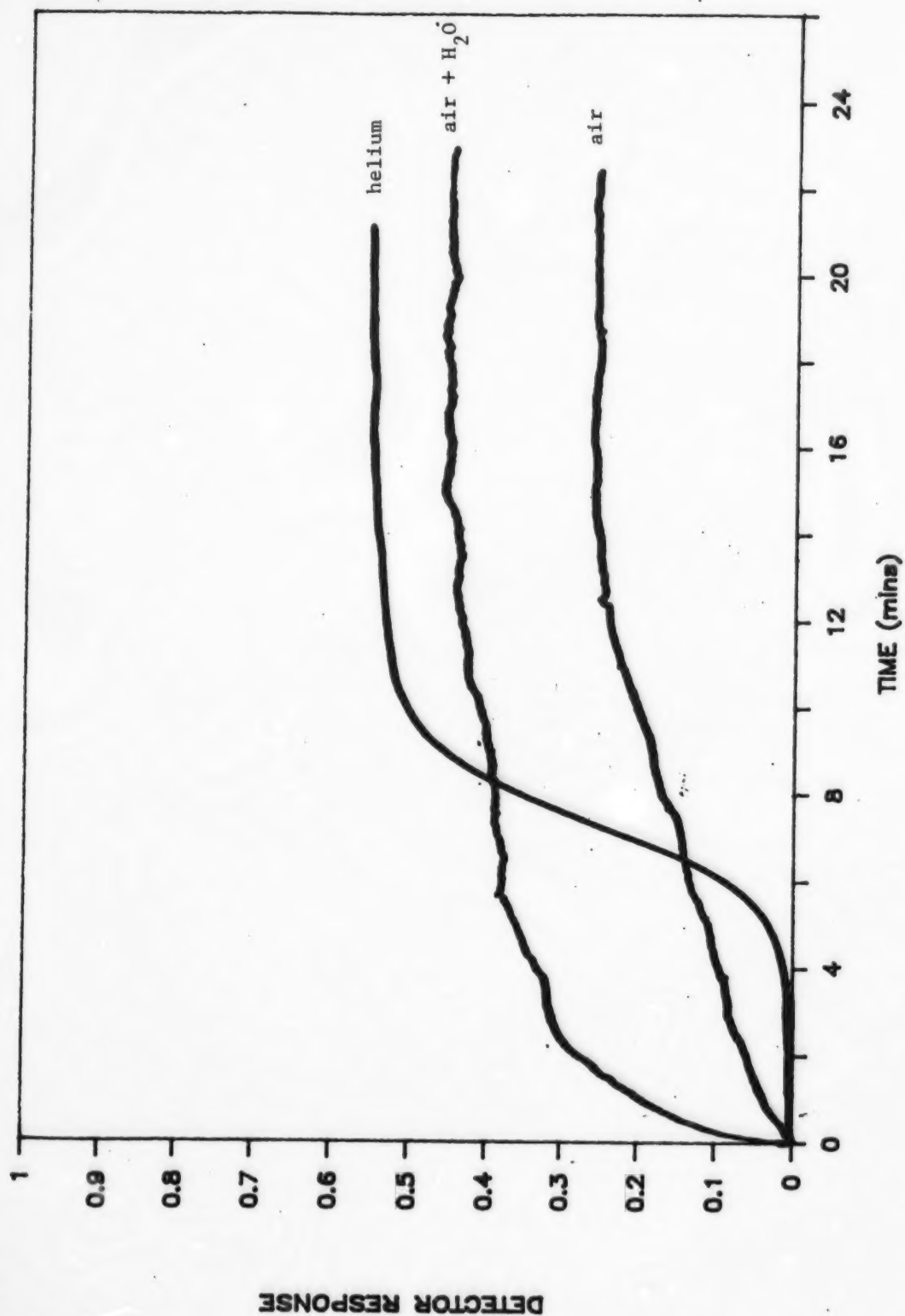


Figure 11: Breakthrough curves of bromoethane from three mixtures of bromoethane-helium, bromoethane-air-water and bromoethane-air.

5.2.2 Regeneration of YAO Adsorbent

Several techniques were employed for the regeneration of YAO adsorbent. These included regeneration by air purge at 33°C and 150°C, and vacuum regeneration by vacuum alone and vacuum plus heating. The results with these methods are summarized in Table 5. As expected air purge at 150° is the fastest method of regeneration. Unfortunately, this technique is not possible to use in a treatment facility since only air from the chamber is available to blow over the bed.

Vacuum desorption was effective at room temperature but only for the finer particle size (40 x 60) mesh. For the 4x8 mesh material it appears that diffusion processes make desorption by vacuum only effective when the adsorbent bed is at temperature greater than 100°C.

Table 5 Summary of Regeneration Technique for YAO

Method	Particle Size	Duration	Wt% Bromoethane		Pressure	Temp.
	(mesh)	(hrs)	Initial	final	(μ m Hg)	(deg C)
Air purge	40x60	16	57.3	11.3	760 K	33
Air purge and heat	40x60	4	57.3	0.0	760 K	33
Vacuum	40x60	4.5	57.3	3.6	31	23
Vacuum	4x8	12	15.0	13.4	60	23
Vacuum and heat	4x8	12	27.5	0.0	140	> 100

5.2.3 Bench Scale Experiments

The objective of this set of experiments was to determine the concentration of bromoethane in the exposure chamber after the gas had been circulated through a bed of YAO activated carbon and equilibrium had been achieved. In this way a check of the results of the screening experiments could be made using an independent method and by monitoring the chamber contents as a function of time, the kinetics of adsorption could also be measured. Table 6 provides a summary of these experiments. Included in this table is the initial concentration of bromoethane in the chamber and the concentration after adsorption, the adsorbed phase concentration and the time required to reach equilibrium as well as the temperature. Plotted in Figures 13 to 18 is the concentration of bromoethane in the chamber (mol %) as a function of time.

Figure 12 shows the good agreement of the equilibrium isotherms obtained using the small bench scale apparatus at 23°C and the isotherm obtained from the screening experiments at 33°C. The small difference between the two isotherms at the point they overlap can be accounted for by the difference in temperatures.

Mixtures of bromoethane in air and in air with water at 90% relative humidity were prepared for experiments 3 and 6. The results show that the adsorbed phase concentration of bromoethane is reduced slightly by the presence of water

from 21.9 to 20 weight percent and is similar to the results obtained in the screening studies.

Analysis of the kinetic results indicate that the rate of adsorption is reduced by the presence of water; in experiment 6, the equilibrium concentration in the chamber was achieved in 27 minutes and in experiment 3, 16 minutes was required for the bromoethane concentration in air to achieve equilibrium.

The practical implications of these results suggest that although the adsorbed phase equilibrium may only be reduced slightly by a high concentration of water, the slow rate of adsorption must be allowed for and a longer residence time in the adsorption bed is required.

Table 6: Summary of Small Scale Adsorption Tests

EXPT.	Bromoethane Injected (grams)	Bromoethane conc. in air		Bromoethane adsorbed		Equilibrium reached *** (mins)	Temp. (C)
		initial (mol%)	equil. (mol%)	initial (wt%)	equil. (wt%)		
1	26.78	2.220	<0.001	0.0	9.9	15	23
2	57.06	5.320	0.158	9.9	30.1	20	23
3	57.50	4.014	0.055	0.0	21.9	16	23
4	39.97	2.780	0.018	0.0	15.0	12	23
5	82.85	5.750*	0.556	15.0	42.7	20	23
6	55.70	3.890*	0.081	0.0	20.0	27	27****

* estimated initial concentration

** time at which first minimum bromoethane concentration reading reached

**** water vapour presence at 90% relative humidity

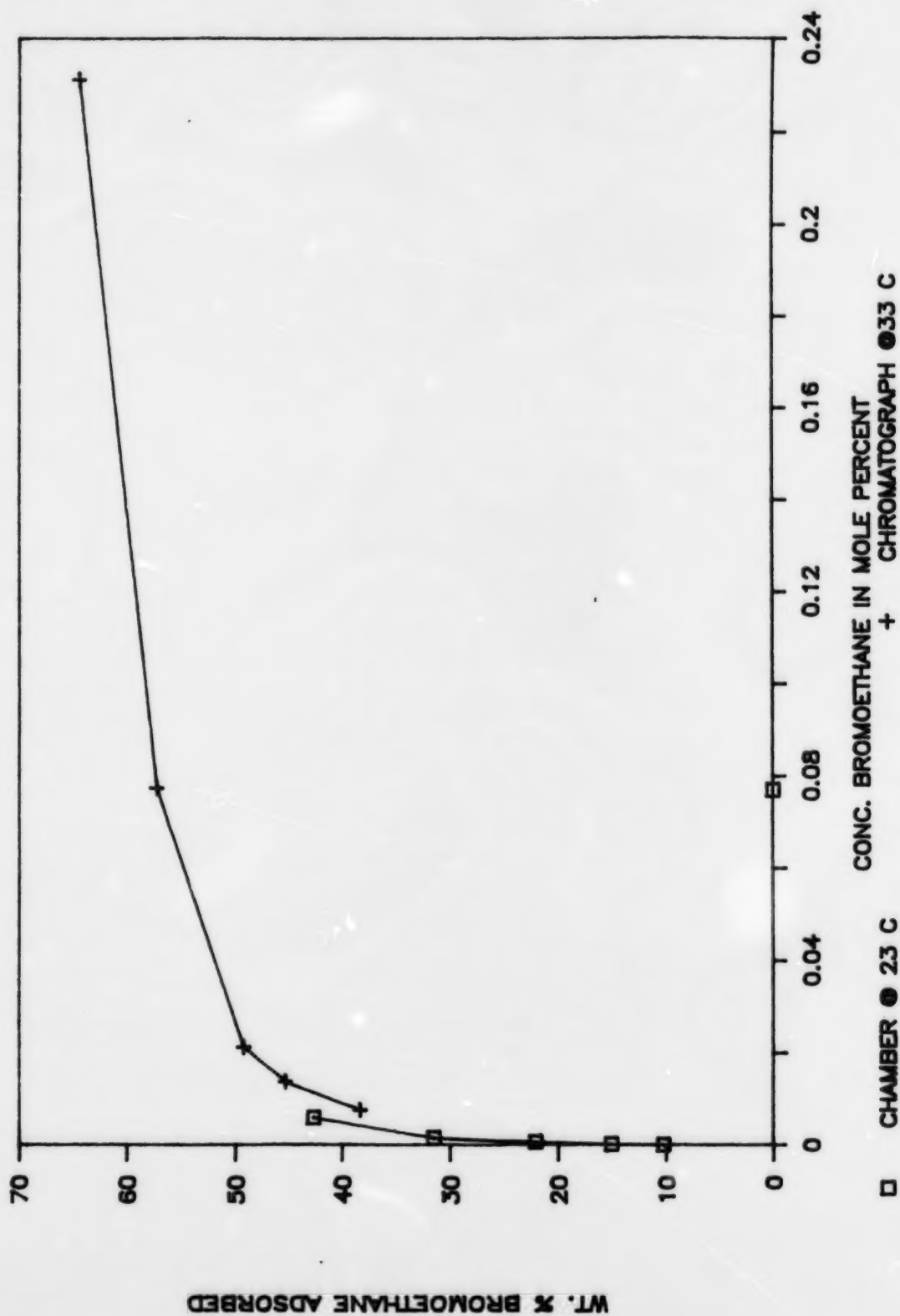


Figure 12: Adsorption equilibrium isotherms for bromoethane on YAO at 23°C determined using the small bench scale apparatus and at 33°C determined using the screening studies apparatus.

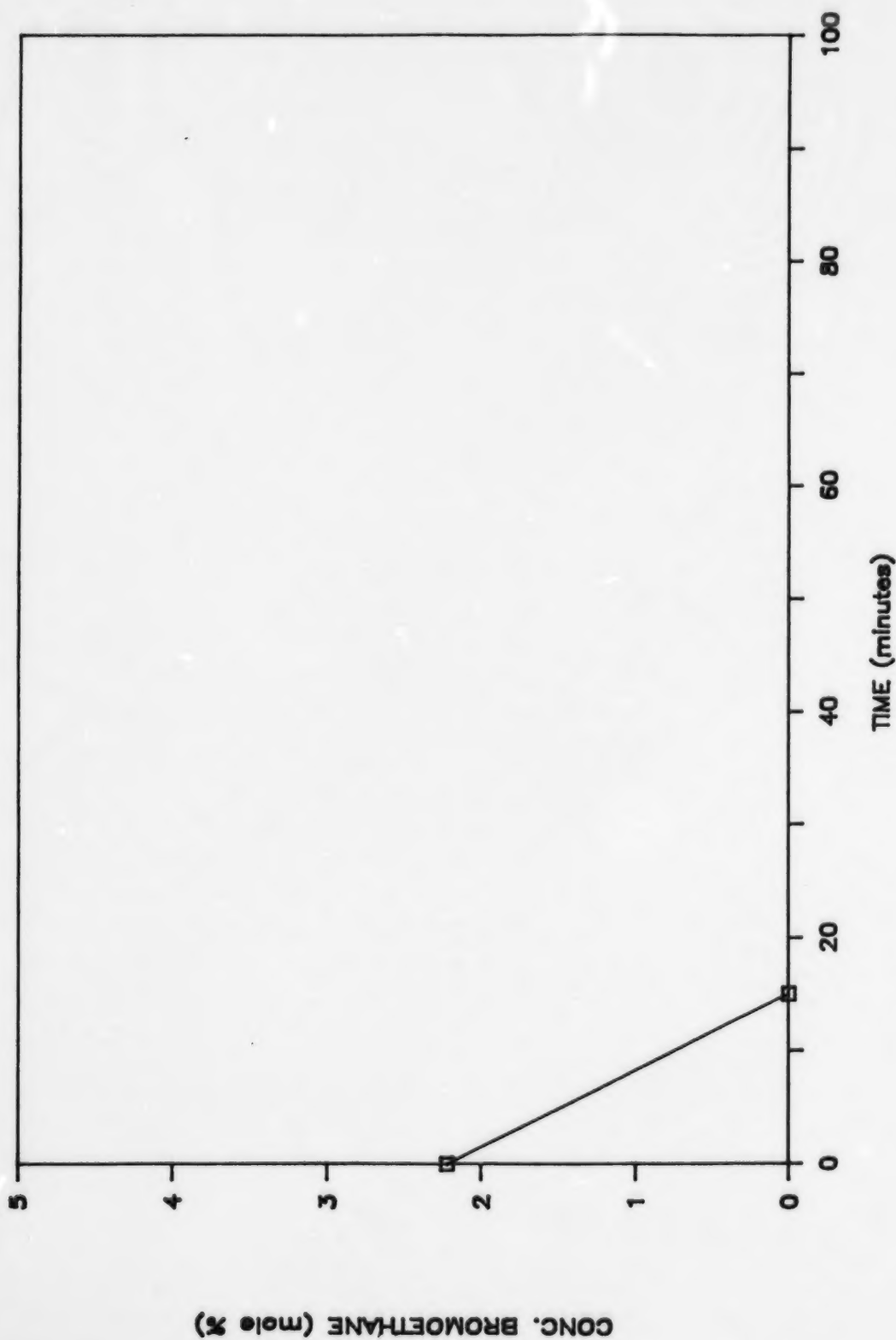


Figure 13: Bromoethane concentration in the chamber of the bench scale apparatus as a function of time using an initial concentration of 2.2 mol% bromoethane in air.

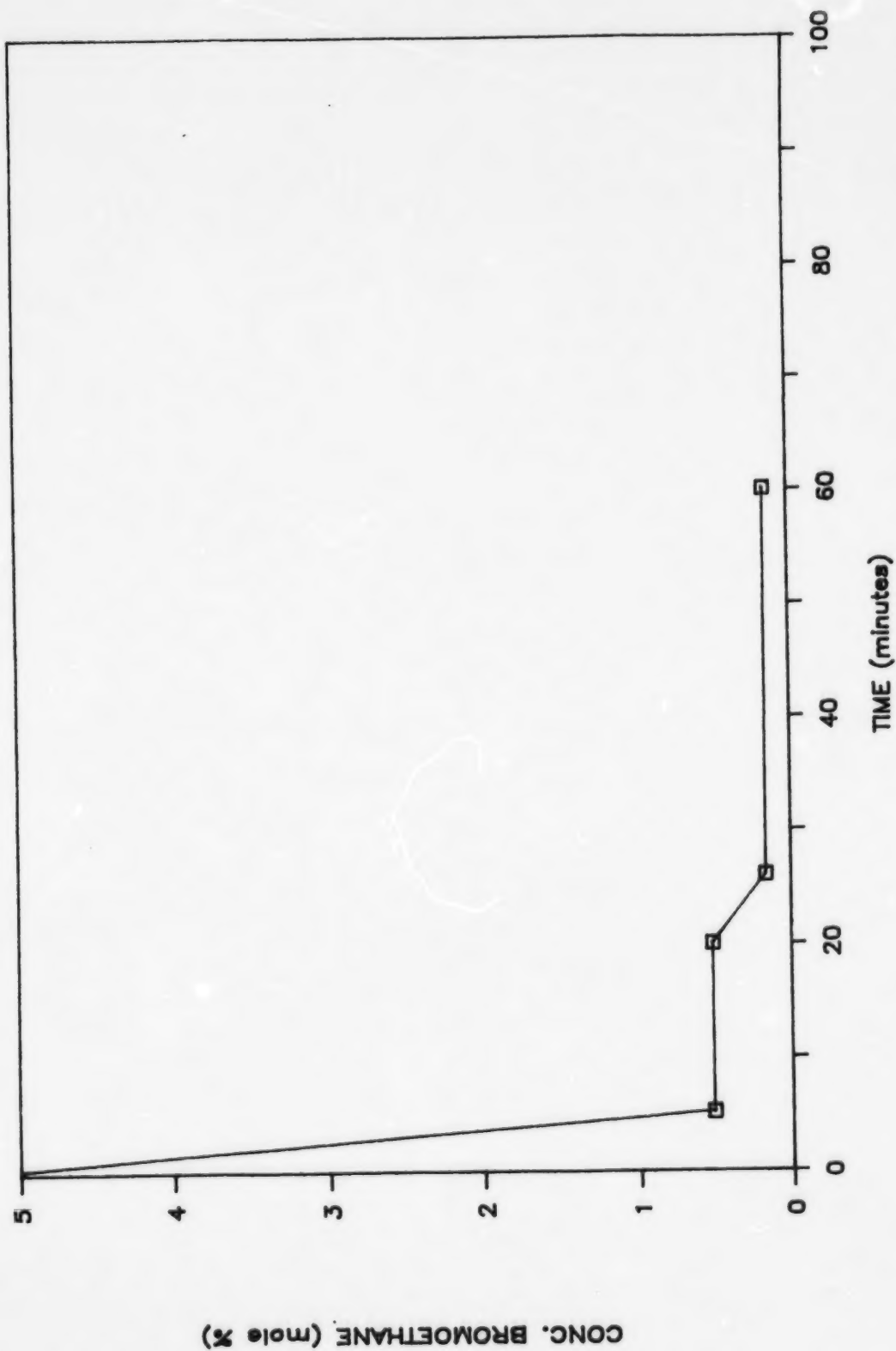


Figure 14: Bromoethane concentration in the chamber of the bench scale apparatus as a function of time using an initial concentration of 5.3 mol% bromoethane in air.

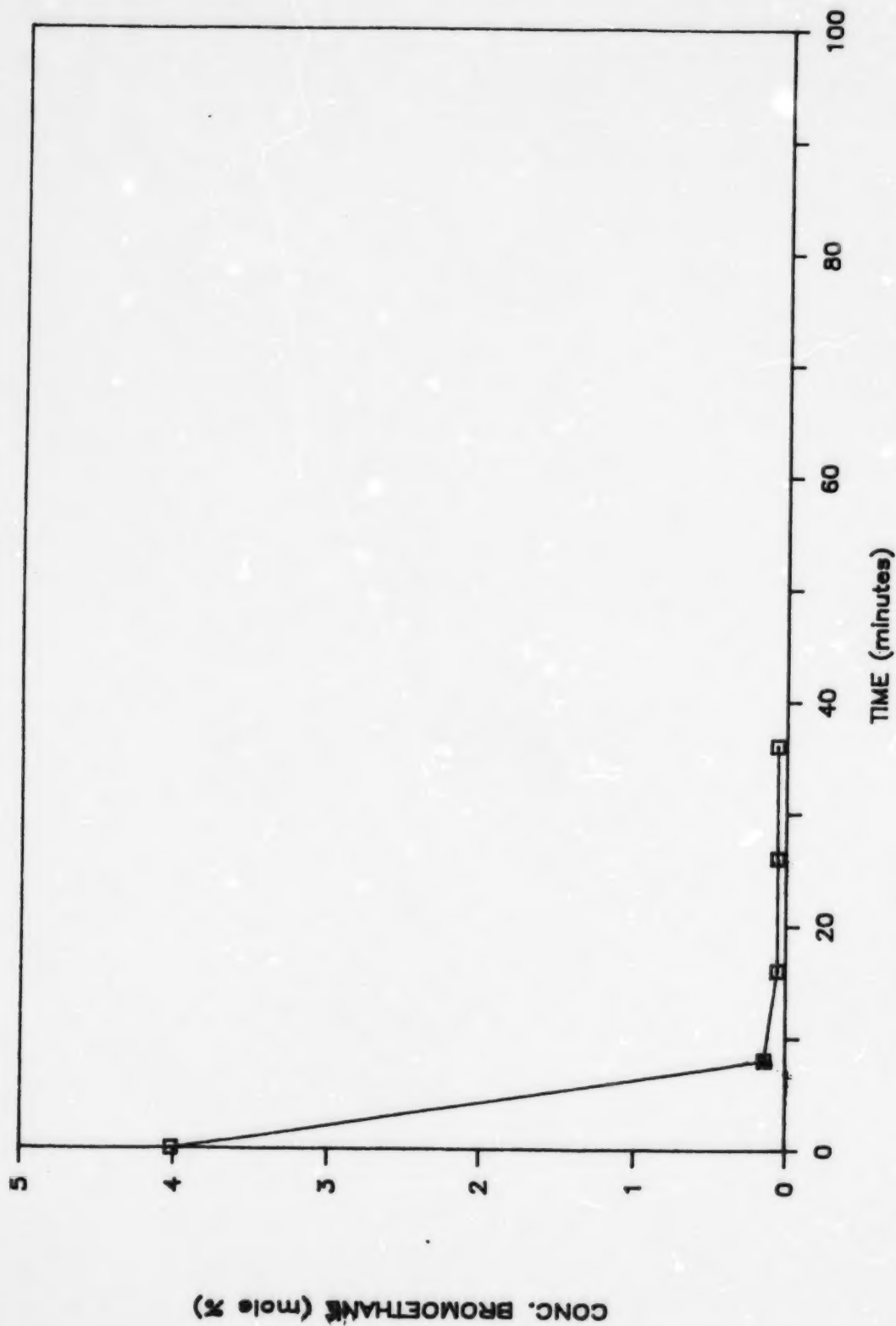


Figure 15: Bromoethane concentration in the chamber of the bench scale apparatus as a function of time using an initial concentration of 4.0 mol% bromoethane in air.

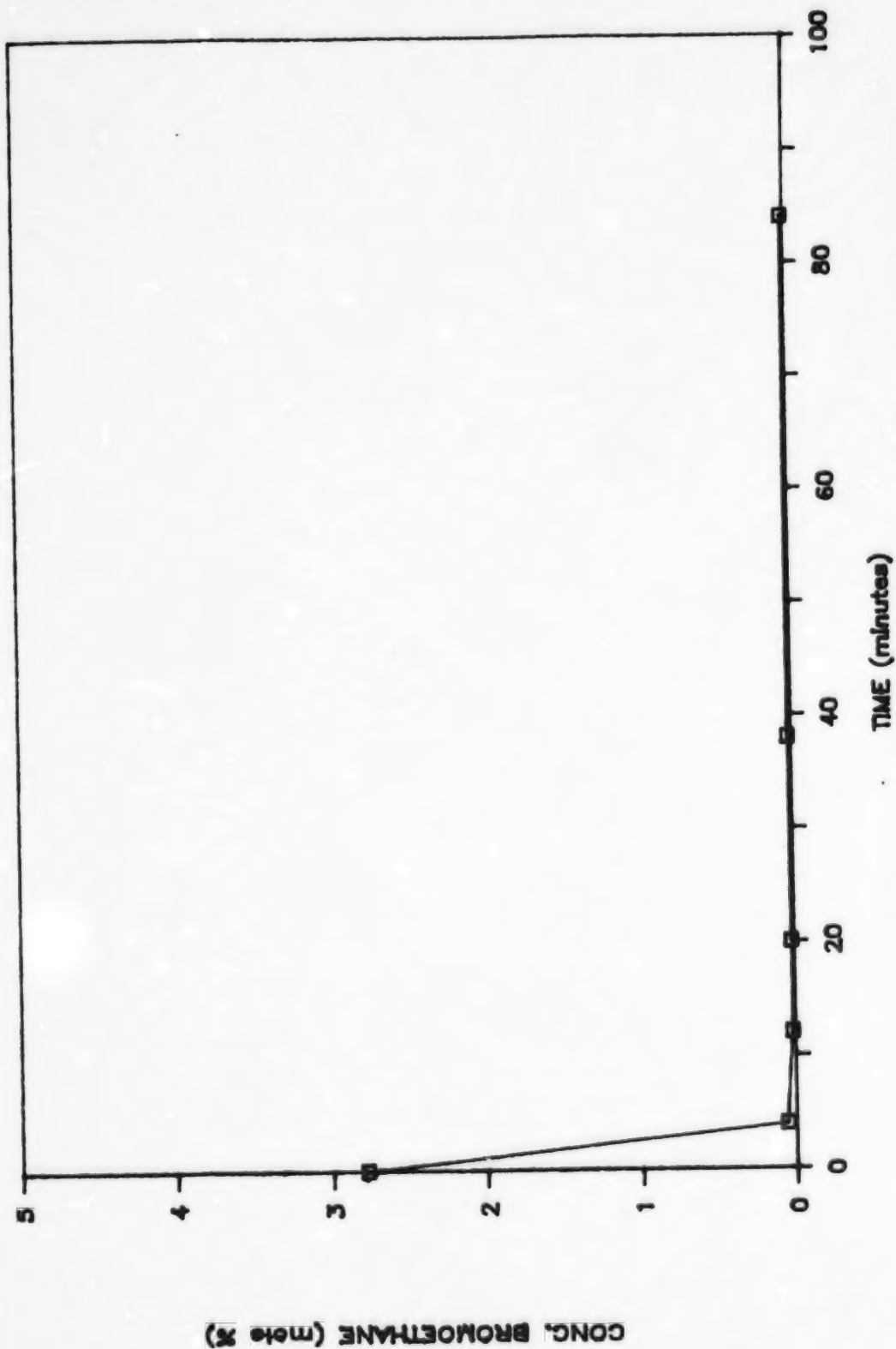


Figure 16: Bromoethane concentration in the chamber of the bench scale apparatus as a function of time using an initial concentration of 2.78 mol% bromoethane in air.

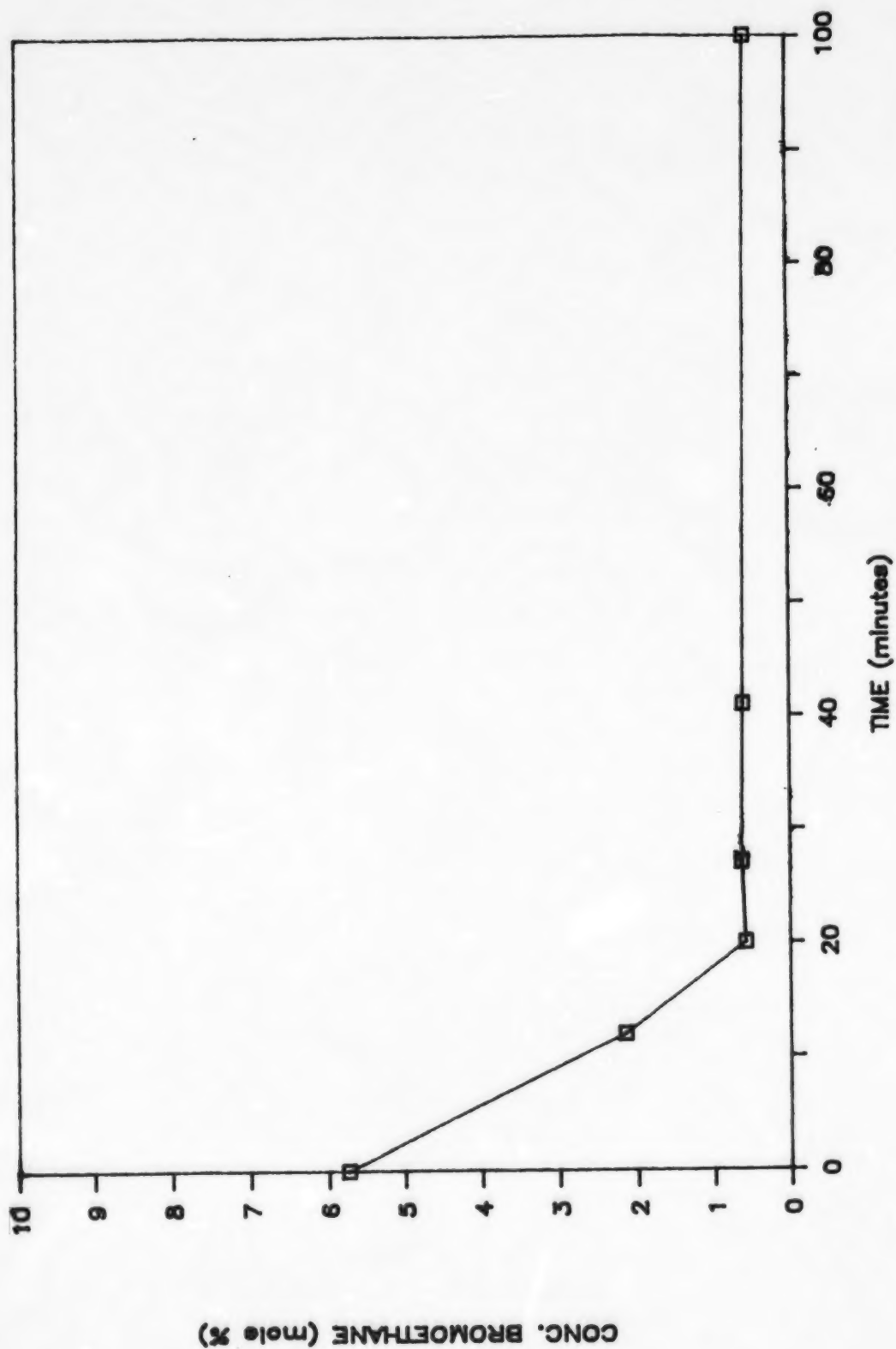


Figure 17: Bromoethane concentration in the chamber of the bench scale apparatus as a function of time using an initial concentration of 5.8 mol% bromoethane in air.

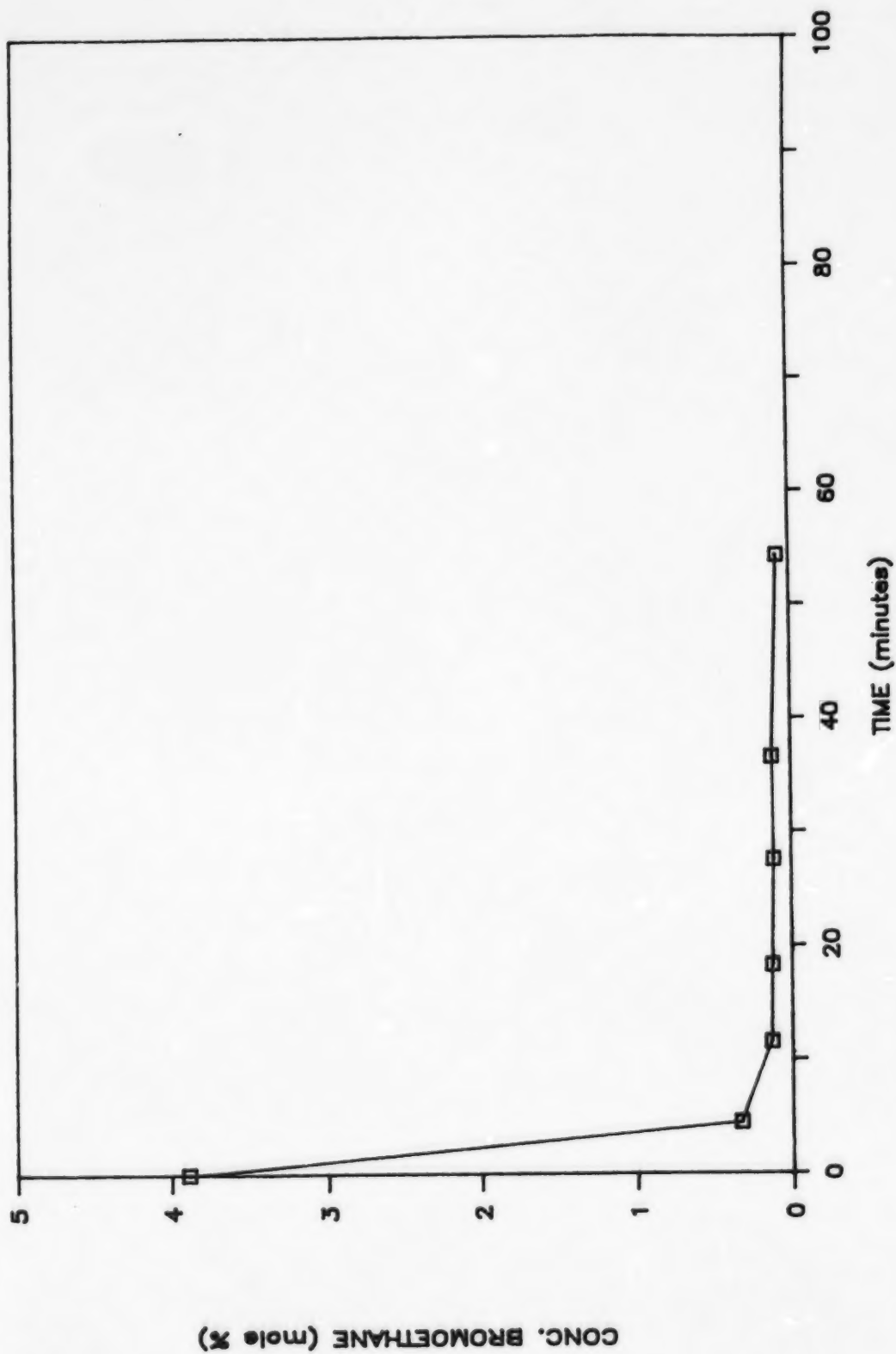


Figure 18: Bromoethane concentration in the chamber of the bench scale apparatus as a function of time using an initial concentration of 3.81 mol% bromoethane in air.

VI CONCLUSIONS

1. The adsorption with reaction system is an inappropriate technology for handling bromoethane from an environmentally safe and engineering convenience point of view.
2. Results of the screening studies for adsorbents indicate that both YAO and HTO activated carbon have a high capacity for bromoethane that is essentially the same. The more economic YAO is the adsorbent suggested for an adsorption system for handling bromoethane.
3. Water vapour in a mixture of bromoethane and air will only reduce the equilibrium concentration of adsorbed bromoethane slightly. The rate at which bromoethane equilibrium is achieved is reduced by the presence of air and water.
4. The low heat of adsorption (5.4 kcal/mol) indicates that heating or mild heating with vacuum will desorb bromoethane from the activated carbon.

VII RECOMMENDATIONS

7.1 Introduction

The adsorption system is an appropriate technology for handling bromoethane in a treatment facility to break the dormancy period of seed potatoes. Since the effects of compounds released from the adsorption capacity is not well understood or the flowrate of bromoethane determined to achieve an optimal time for equilibrium to be achieved a pilot plant is recommended.

7.2 Pilot Plant Facility

The pilot plant is envisaged as two fixed beds with regeneration by vacuum and heating. Both beds in the system will be of equal size with an over design allowance of 25% for bromoethane capacity. All functions of the adsorption-recovery system are monitored and regulated by a computerized control system. A schematic diagram is presented in Figure 19.

Bromoethane is introduced to the chamber via an automated dispensing and evaporation system. The tubers are then exposed for the required time.

In the first stage of the bromoethane adsorption cycle, air from the chamber is to be blown through bed #1. This continues until the bromoethane concentration in the chamber falls to an equilibrium level, i.e. approximately 85% of the bromoethane is recovered. At this point, bed #1 is isolated and bed #2 is opened to the system. Air circulation through

bed #2 is continued until the bromoethane concentration in the chamber falls below the 200 ppm threshold level. Then bed #2 is isolated from the chamber.

The treated tubers are removed and the chamber is reloaded. Release of the bromoethane to the chamber is accomplished by heating of the bed to 150°C and imposing a vacuum. Any additional bromoethane required because of leakage or adsorption by the tubers is added by the automated dispensing system. Spent activated carbon after a number of adsorption cycles may be transferred pneumatically (using the blower) to containers for disposal.

A summary of the costs of materials for a pilot plant system is presented in Table 7 and the basis for this calculation is found in Table 8. It should be noted that quoted costs do not include: a. delivery charges, b. installation, c. labour and technical assessment costs.

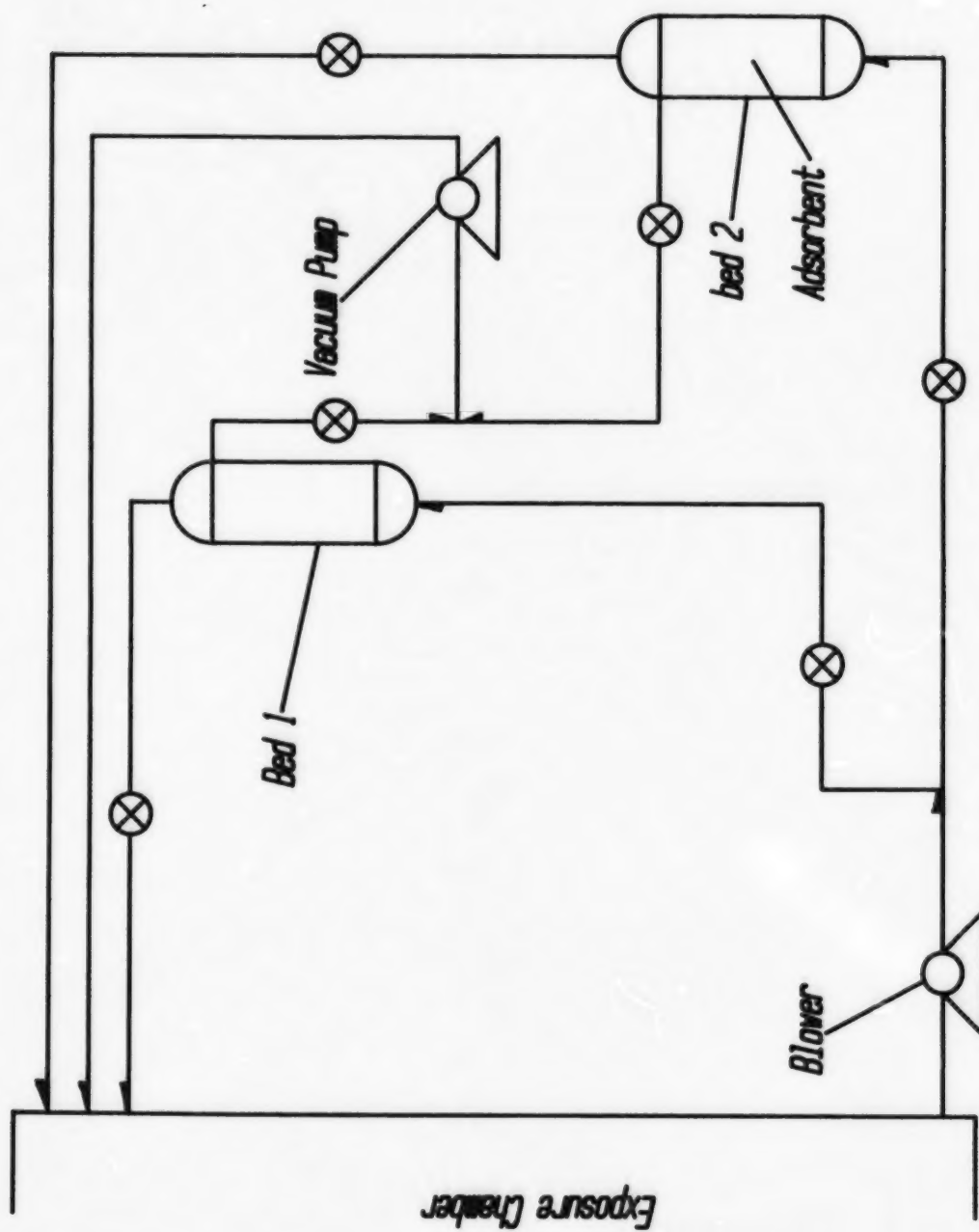


Figure 19: A schematic diagram of an adsorption pilot plant for handling bromoethane.

Table 7: Pilot Plant Materials and Costs

Item	detail	quantity	unit cost	price
Adsorbent system	2 - SS, 3'dia x 4', stands 4 - 250 mm SS vac valves 2 - 40 MM SS vac valves 1 - 40 cfm vac pump heaters, T/C's, controller vac sensors and display system controller			\$100,000
activated carbon	YAO 6x16 mesh	350 kg	\$ 3.50	\$ 1,225
Blower	1200 cfm, FRP	1	\$ 5,600	\$ 5,600
Compressor	for pneumatics	1	\$ 1,000	\$ 1,000
Piping	to adsorber beds, circulation	1	\$ 9,000	\$ 9,000
Circulating fans	for air mixing in chamber	2	\$ 1,500	\$ 3,000
Air filter system	for adsorption system	1	\$ 5,000	\$ 5,000
Control system	computer + relays			\$15,000
Bromoethane dispensor	pump, control valve, tank, evap	1	\$ 4,500	\$ 4,500
Bromoethane detector	B & K model 1302 0.8 to 80000 ppm	1	\$34,700	<u>\$34,700</u>
component total				\$179,025

The cost estimate provided is for a demonstration scale pilot plant. Because of the time restrictions that may be placed upon construction and commissioning of the plant the major components i.e. adsorbent, beds, valves and vacuum system have been priced as a manufactured unit. Due to the high capacity of the activated carbon for most organized compounds and the flexibility of the vacuum/heat regeneration regime, it is anticipated that the facility may be capable of handling other types of toxic agricultural fumigants.

Table 8: Basis for Pilot Plant Calculations

BASIS. BROMOETHANE: 55.2 kg
 BROMOETHANE @ 4 MOLE%
 CHAMBER VOLUME: 283.5963 M³ 10017 cuft

Bed #1 for adsorber bed assume 40 wt% adsorbed on bed #1
 and equilibrium b/e concentration of 0.60 @ 23 dec C
 bed designed with 25% additional capacity

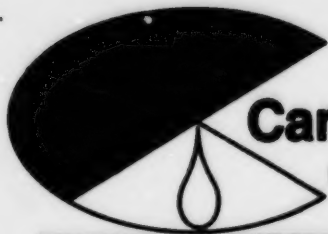
bulk density of adsorbent	440 kg/m ³	
weight of adsorbent in 1	172 kg	
volume adsorbent	0.391 m ³	13.8 cuft
bed diameter	0.92 m	3 ft
bed length	0.37 m	1.20
face velocity	0.51 m/s	100 fpm
blower capacity	0.47 m/s	1000 cfm
air changes/hour chamber	5.99	

Vacuum system:

target vacuum	50 microns Hg
volume B/E adsorbed	11344 liters
capacity	850 liters/min
pump down to target	2.67 hours

Bed #2 bed size is the same as #1. This is probably cost
 effective if vessels are custom built. The criteria that
 the second bed must meet is to have enough capacity to
 remove remaining bromoethane from chamber after bed #1
 reaches equilibrium and is switched out of the
 recirculating mode. The remaining bromoethane in the
 chamber when bed #2 is switched in should be less than 10
 weight percent of the adsorbent in bed #2. Based on lab
 scale test the remaining bromoethane should be less than
 15% of the original. This would be 8.28 kg making a
 minimum bed size of 82 kg. A reasonable safety margin is
 thus maintained by making bed #1 and #2 of equal size.

APPENDIX I: Physical Properties of Adsorbents



Carbon and Filtration Products Company

P.O. Box 41, Station "A", Islington, Ontario M9A 4X1 Phone (416) 251-3888 Telex: 08-984711

ACTIVATED CARBON

Applications

Even very broad classification of applications into Gas Adsorbency & Decolorising does not do justice to the manifold uses of Activated Charcoal.

The undemoted list hardly illustrates the extensiveness of the individual applications within some of the basic areas described.

- Industrial Gas Masks
- Solvent Recovery in various Industries
- Purification of Glucose
- Military Gas Masks
- Manufacture of Pharmaceuticals
- Odour Removal in Cooker Hoods
- Decolourisation of Mineral, vegetable & Animal Oils
- Military Clothing
- Medicinal Applications
- Recovery of Precious Metals from Ore
- Treatment of Alcoholic Beverages
- Air Conditioning Domestic Industrial Naval/Aircraft
- Veterinary Applications
- Dechlorination & Purification of Water Domestic Water Filters Municipal Water Filters Mineral Water Factories & Breweries
- Aquarium Filters
- Toxic Gas Exposure Personal Sensors
- Agricultural Applications
- Adsorption of Radioactive Gases in Nuclear Plants
- Industrial Water/ Effluent Treatment
- As a Catalyst or Catalyst Support
- Foot Pads for Odour Removal
- Purification of CO₂ in Mineral Water Factories
- Purification of Dry Cleaning Solvents
- Purification of Electrolytes
- Evaporation loss Control in Autos
- Decolourisation of Sugar
- Cigarette Filters



Carbon and Filtration Products Company

P.O. Box 41, Station "A", Islington, Ontario M9A 4X1 Phone (416) 251-3888 Telex: 06-984711

Selection

A number of empirical tests may be used to determine the essential chemical/physical properties of an Activated Carbon as a general guide to preliminary selection or quality control. However, simulated lab trials or pilot plant operation with the actual material to be purified, under process conditions identical to the Industrial Scale, and techno-economic evaluation, are necessary prerequisites to ultimate choice of a specific grade of Carbon, particularly for a new application.

Salient properties - Porosity

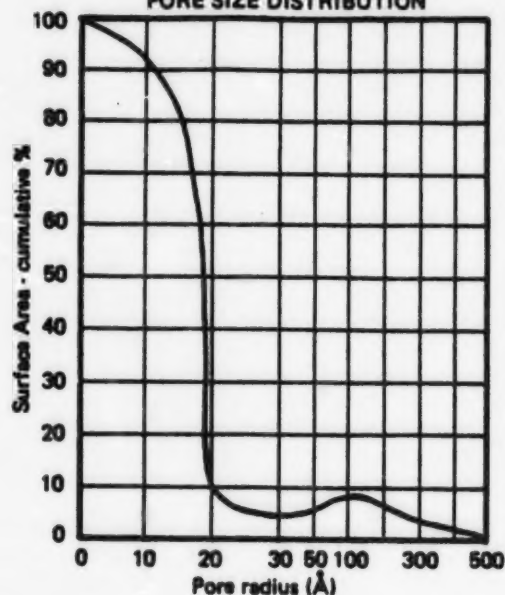
The surface area of an Activated Carbon is determined usually by the "B.E.T." (Brunauer S, Emmett P.H., & Teller, E) method employing either Benzene or Nitrogen. Whilst being a reasonable indicator of total potential adsorptive capacity, it must be related to pore size distribution for a more accurate determination of potential capacity for specific adsorbates. The micropores ranging usually from 5 Å to 40 Å perform the actual adsorptive function, whilst the larger ones act as access routes to these adsorption sites or are responsible for adsorption of large colour bodies.

Adsorption

In more practical terms, for gas phase applications the industry has adopted known vapours/gases such as Benzene at various saturations, Carbon Tetrachloride, Acetone, Toluene, etc, etc, as standards to assess adsorptive capacity for adsorbates of different molecular weights. Whilst varying test methods and conditions are in existence, the basic principle is for the gas in a specified concentration, to be passed through a known weight of Carbon until saturation of the latter is reached. The result is expressed as a percentage by weight of gas adsorbed over weight of Carbon taken.

In certain applications, the retentive capacity of a Carbon for adsorbed vapour is also (or more) important. This is assessed by passing clean air through the vapour saturated bed of Carbon to constant weight of latter, and determining the amount of vapour remaining adsorbed onto the Carbon. The amount "desorbed" is of relevance to some users, especially solvent recovery.

TYPICAL GAS PHASE CARBON
PORE SIZE DISTRIBUTION

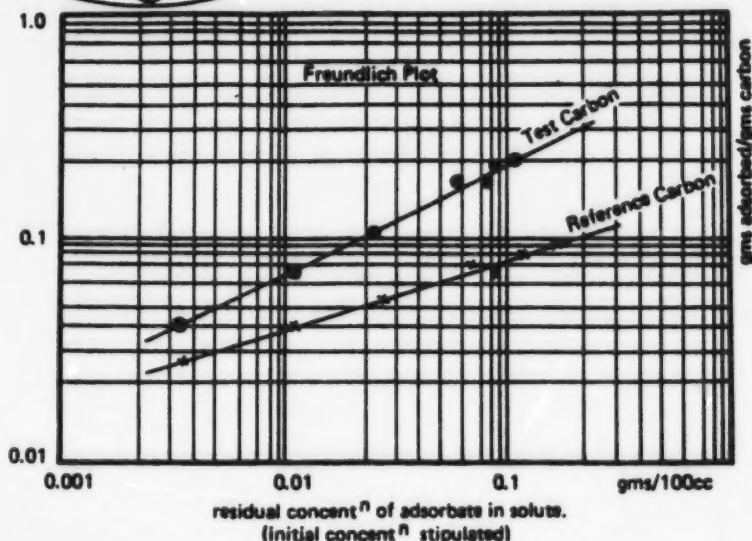


Liquid phase applications in the typical decolourising field, use Meth. Blue or standard molasses solutions, whilst in water purification, Phenol or Iodine values are used. In most instances the capacity being related to percentage colour adsorbed per 100-gms. of Carbon or, conversely, the amount of Carbon needed to reduce known initial concentration of adsorbate to a specified level. The use of the Freundlich adsorption isotherm reflects quantum adsorbed per 100-gm. of Carbon versus quantum left unadsorbed in the solute at constant temperature.



Carbon and Filtration Products Company

P.O. Box 41, Station "A", Islington, Ontario M9A 4X1 Phone (416) 251-3888 Telex: 06-984711



The Freundlich equation is:-

$$\frac{a}{c} = K \times B^{1/n}$$

Where a = quantum adsorbed
 c = Carbon used
 k = constant
 B = Concentration in solute after adsorption
 i / v = constant

If the results are plotted logarithmically, straight isotherms are obtained.

Dechlorination applications specify "Halving values" which refer to the height of the Carbon layer in a filter needed to reduce the inlet chlorine concentration in water by 50%, under described conditions of water quality & temperature. Dechlorination is a catalytic reaction. The foregoing are generalisations and it has been our experience that customers often specify (and expect to be provided data on) other test methods or parameters closer to reflecting conditions of their individual applications. For example, in the recovery of Precious Metals From Ores, a number of alternative laboratory test methods for preliminary evaluation of various Carbons for adsorption, on the one hand, and elution on the other, are used, though pilot or full plant scale results are more conclusive and relevant, especially in the context of the presence of other organic/inorganic material in various pulps, not present in Gold solutions prepared in the laboratory.

Particle size

Pelleted Carbons are identified by their diameter, usually 1, 2 or 4-mm, the length being usually 1-2 times the diameter. Agglomerated forms are designated by their diameter whilst natural Granular Carbon by sieve sizes/ranges, e.g. ASTM 4x8, 8x12, etc. This is expressed in ASTM, BSS, Tyler, mm or other sieve series and it is vital this suffix accompany the numerical description of sieve sizes.

It is generally accepted that Granular material falls within the broad range of 5-mm to 0.30-mm, whilst anything finer is classified as Powder. Coarse powders could thus be ranged as 300 to 100 microns but finer powders are generally designated by the percentage of material retained, or passing through 150 microns (ASTM 100 mesh) or 75 microns (200 mesh), or 45 microns (ASTM 325 mesh). Contrary to what we might expect, particle size, and hence external surface area, makes negligible contribution to the total surface area of a Carbon. It does, however, favourably influence the rate of diffusion, and with it the rate of adsorption. Thus a 'finer' particle sized Carbon of the same total surface area and pore characteristics, would reach equilibrium adsorption faster than a coarse one.

The constraints with regard to particle size is that with Granular fixed bed applications, finer particles present resistances to airflow, or pressure drops in liquid flow, which are often incompatible with purification plant processes. In the batch type contact process, with powders the limitations are filterability. Selection of optimal particle size range, therefore, must be based on above considerations and relative cost benefits. Particle size ranges are determined using Laboratory Test Sieve Shakers and Standard Sieves, but variations have been observed in result depending on test conditions, sampling, and shaker motion, etc.

Commercial screening does not usually permit of the accuracy of distribution or "cut" achieved with laboratory test sieve shaking and thus, manufacturers tend to confine themselves to 3-4 principal size ranges compatible with each other on production and intended for applicational areas. e.g. ASTM 4x10 and 8x16 for Gas phase and 12x30 for Liquid phase.

Particle size - contd.

Tolerance limits of 5% each for over and undersizes are normally allowed although more exacting requirements may specify actual particle size distribution within the broad range, or zero limits on very fine particles. There is no doubt that in wide size ranges, actual distribution is vitally important.

e.g.

+ 5.00 mm	= 0%
5.00 x 4.75 mm	= 05% Max
4.75 x 3.35 mm	= 40-60%
3.35 x 2.35 mm	= 30-50%
2.35 x 2.00 mm	= 05-10%
- 2.00 mm	= 02-03%
(- 1.70 mm	= 0%

Grade designated usually as ASTM 4x10, though it is more typically a 4x8 (4.75mm x 2.35mm).

The Mean Particle Diameter often referred to is computed by multiplying the weight of each size fraction by the mean of its top and bottom sieve openings, and then summing these weighted values for each fraction and representing it as a percentage. In the above, for example, assuming range was 60%, 4.75 x 3.35 and 40%, 3.35 x 2.35, the Mean Particle Diameter is 3.575 mm. "Generally", the coarser grades are employed in Gas and Air Purification Applications and the finer ones in liquid Phase Applications.

Examples of Pressure Drop Charts
(not repete of Haycarb Carbons)

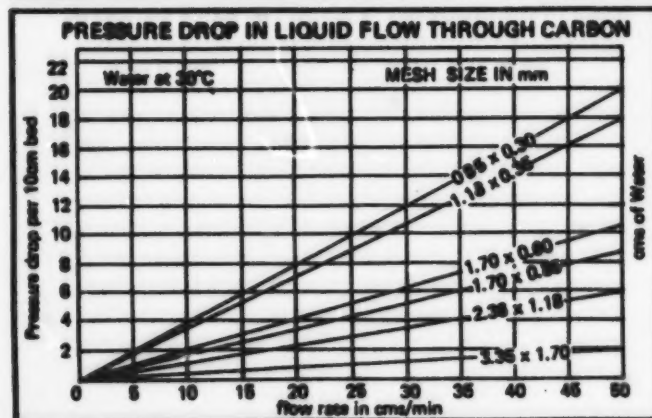
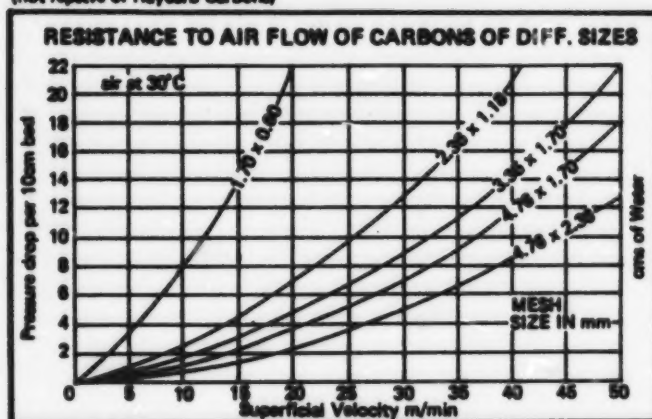


TABLE OF MESH EQUIVALENTS

mm	ASTM E11-70	TYLER	CLOSEST BSS 410-82
5.00	10		
4.75	4	4	3/16 INCH
4.00	4.00	5	
3.35	6	6	5
3.00			
2.80	7	7	6
2.35	8	8	7
2.00	2.00	10	9
1.70	12	10	10
1.40	14	12	12
1.18	16	14	14
1.00	1.00	18	16
0.85	20	20	18
0.71	25	24	22
0.60	30	28	25
0.50	35	32	30
0.42	40	35	36
0.38	45	42	44
0.30	50	48	52
0.21	70	65	72
0.15	100	100	100
0.075	200	200	200
0.045	325	325	350
0			

CANADIAN 8 GP-1b
FRENCH AFNOR X-11-501
GERMAN DIN 4188

SIEVE SERIES
AVAILABLE
ON REQUEST

technical bulletin
fluid processing
chemical



Amberlite® XAD-4 Resin

Amberlite XAD-4 resin is a polymeric adsorbent in the form of white insoluble beads which can be used to adsorb hydrophobic solutes from polar solvents. While it is employed in columns in a manner similar to ion exchange resins, Amberlite XAD-4 differs from ion exchange resins in that it has no ionic functional groups incorporated into its resin structure. Rather, Amberlite XAD-4 is a completely nonionic hydrophobic polymer which derives its adsorptive properties from its macroreticular structure, broad range of pore sizes, unusually high surface area, and the aromatic nature of its surface. A principal use for Amberlite XAD-4

is in the adsorption of water soluble organic substances of relatively low molecular weight from aqueous systems.

Amberlite XAD-4 is a crosslinked polystyrene-type polymer supplied as 20 to 50 mesh beads. It has exceptional physical durability and can therefore be used in column operations with repeated exhaustion and regeneration cycles. Amberlite XAD-4 has excellent hydraulic characteristics in normal downflow systems. It also has good thermal stability and can be used at temperatures as high as 250°C.

333

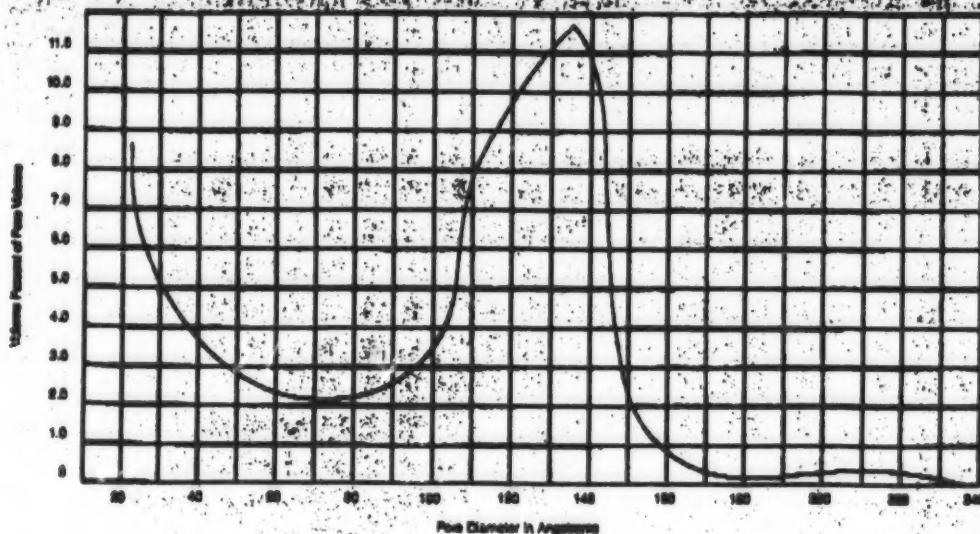
typical properties

Appearance	Hard, hydrated, opaque beads
Average particle diameter	0.35 to 0.45 mm
Harmonic mean particle size	0.45 to 0.60 mm
True wet density	1.03-1.04 gram/ml
Skeletal density	1.08-1.09 gram/ml
Shipping weight	44 lbs/ft ³
Hydraulic expansion	See Figure 1
Pressure drop	See Figure 2

The following properties were determined for dried resin.

Porosity of beads	0.50 ml pore/ml of bead
Surface area	approximately 800 square meters/gram
Average pore diameter	40-60 Angstrom units
Pore size distribution	See Figure 3

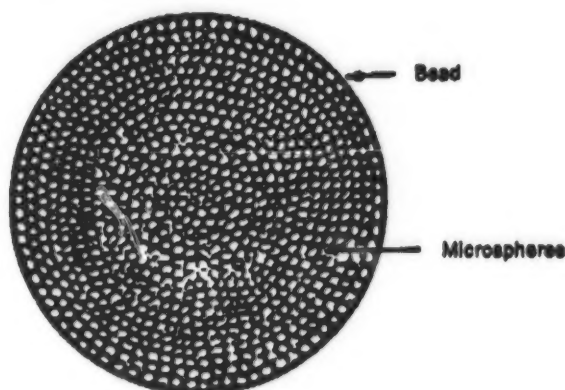
Figure 3. typical pore size distribution of Amberlite XAD-4 by nitrogen desorption isotherm.



process of adsorption

The highly aromatic, and consequently hydrophobic, structure of Amberlite XAD-4 imparts to it an affinity for the hydrophobic portion of organic molecules. The adsorption of these species onto Amberlite XAD-4 occurs, not through ion exchange, but through van der Waals' interactions, the binding ability of which

is a function of the relative hydrophobicity of the solute, the solvent and the adsorbent. To better understand the phenomena through which Amberlite XAD-4 functions, consider the individual beads to be an agglomeration of a large number of very small microspheres, fused together into a spherical agglomerate. This is depicted in the sketch below.



The macroporous structure results in a continuous solid phase as well as a continuous void, or pore, phase so that water, or other solvent, can very readily penetrate the pores. This type of structure results in a very high surface area in each bead.

In adsorption, that portion of the organic molecule with less affinity for water (or other polar solvent), that is, the hydrophobic portion, is preferentially adsorbed onto the hydrophobic surface of the adsorbent, while the hydrophilic portion of the molecule remains oriented in the

APPENDIX II: Details of Pilot Plant Equipment

High Vacuum Systems Inc.

8040 Shawson Drive
Mississauga, Ontario, Canada L5T 1P5
(416) 673-9310 FAX: (416) 673-9444

QUOTATION

To: University of New Brunswick
Department of Civil Engineering
Fredericton, New Brunswick
E3B 5A3

Attention: Jeff McInerney

DATE: Mar. 10, 1989

QUOTE NO: Q89013.A

QUOTE VALID: budget

F.O.B.: Mississauga

We are pleased to quote the following:

QTY	DESCRIPTION	PRICE
two	Vacuum Vessels including:	
	- Two stainless steel chambers with all required ports, mounted on painted, mild steel frames - Internal supports for adsorbent - Four, electropneumatically operated, 250 mm, all stainless steel, butterfly, vacuum valves, located on inlet and exhaust of each chamber. - Two, electropneumatically operated, 40 mm, all stainless steel, angle valves, one each located on vacuum pumping port of each chamber. - Vacuum pressure sensor and display for chambers. - One 40 CFM mechanical vacuum pump with particulate trap located and connected by a vacuum T to pump either or both chambers. - Insulated heating jackets of sufficient power to heat adsorbent to 200 degrees C. - Six, type T thermocouples for monitoring adsorbent temperature, three in each chamber. - Controller with setpoint to control heating of either chamber. - System controller with PLC/mimic panel and push-button actuation to activate valves and pump.	

BUDGETARY PRICE RANGE \$ 90,000 TO \$110,000

High Vacuum Systems Inc.

NOTE

The price range indicated here is for budgetary purposes only.

TERMS AND CONDITIONS

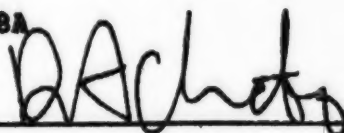
HVSI's standard terms and condition of sale apply to this quotation.

TAXES

Prices are in Canadian Dollars, Federal and Provincial Taxes are extra as applicable.

DELIVERY

TBA



David Chato Manager, Sales

Why photoacoustic spectroscopy?

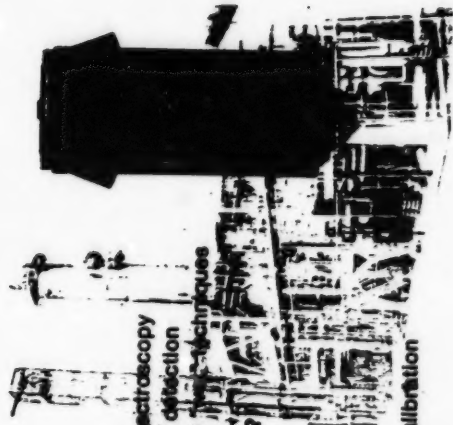
Because it's:

- faster than gas chromatography
- cheaper than mass spectroscopy
- more sensitive than transmission spectroscopy
- more selective than electrochemical detection
- and much more convenient than any other techniques

Why the Toxic-gas Monitor Type 1306?

Because it:

- uses no expendable materials
- offers complete reliability
- needs minimal supervision
- seldom requires maintenance and calibration
- and is cost-effective!



About the company...



Brüel & Kjær

WORLD HEADQUARTERS: DK-2650 Naerum, Denmark. Telephone: +45 2 90 06 00. Telex: 37316 Bvula dk.

London: (01) 462 3333. Athens: 02152/7350-0. Belgium: 02 242 97 43. Brazil: 248 8148. Canada: (514) 694-4225. France: (01) 69 37 044. Federal Republic of Germany: (030) 69 12 286. Hong Kong: (2) 462 38 884. India: (011) 642 38 884. Italy: (02) 52 44 141. Japan: (03) 432-4213. Mexico: (05) 52 51 71 51. New Zealand: (04) 479 1515. Norway: (02) 51 51 51. Singapore: 225 8833. Spain: (01) 246 10 00. Sweden: (08) 7112 730. Switzerland: 0421 66 11 81. Taiwan: (02) 712 8300. USA: (617) 661 7020. U.S.A. representatives and service organizations world-wide.

ISO 9001 CERTIFIED • ISO 9002

Toxic-gas Monitor Type 1306



Early detection is the best protection

Brüel & Kjær

BO 0446-11

Toxic-gas Monitor Type 1308

About the monitor

The Toxic-gas Monitor Type 1308 combines innovation with proven technology to bring unprecedented accuracy to long-term monitoring of toxic gases. It is unique in its use of photoacoustic spectroscopy (PAS), a well established technique applied for the first time to commercially available gas monitors. PAS gives greater sensitivity than infra-red spectroscopic methods, yet has the same advantages — it uses no expendable materials, gives a fast response and is reliable. The sensitivity of PAS allows constant monitoring of process emissions — giving warning of potential hazards before they arise — keeping you in touch with the safety level of your plant at all times.

The monitoring network

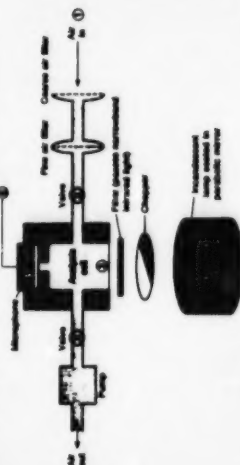


The Toxic-gas Monitor is fully automated and remote-controlled from a personal computer; user-friendly software is available for simple control and easy data analysis. The monitoring system can be large or small, depending on your requirements.

In short, the Toxic-gas Monitor and its communication system provides for a complete, flexible monitoring network that requires minimum attention and maintenance, whilst ensuring safety for your personnel and property.

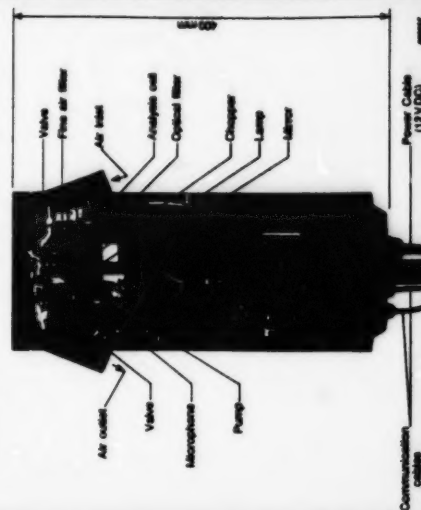
The measurement procedure

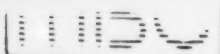
The measurement principle used by the Toxic-gas Monitor is Photoacoustic Spectroscopy. This is the measurement of the acoustic wave generated by a gas when it absorbs modulated light. The wavelength of the light determines which gases are detected; the wavelength is altered by fitting one of the many optical filters available, covering the infra-red spectrum.



Measurement Sequence

1. air is drawn into the analyte cell and the cell is sealed
2. radiation from the lamp passes through a chopper and optical filter, then enters the analyte cell
3. if present in the air, the specified gas absorbs light and generates heat, thereby increasing the pressure in the cell
4. the pressure increase is periodic at the light-chopping frequency and so it simply a sound wave which is detected by the microphone
5. the microphone signal, which is proportional to the gas concentration, is processed and the result transmitted to the central control station





metabyte
Corporation

DATA ACQUISITION AND CONTROL FOR IBM PC/XT/AT, COMPATIBLE AND VME BASED COMPUTERS

MDI-16/MSS-16 16 CHANNEL SOLID-STATE I/O MODULE SYSTEM FOR THE METRABUS

FEATURES

- Easy to use
- Up to 512 Digital I/O modules
- Up to 32 I/O mounting racks
- Control up to 3 AMP AC & DC loads
- Sense AC & DC signals
- Easy programming with INP & OUT BASIC statements
- Detailed operator's manual with example programs
- Up to 1500V isolation
- Can be powered from PC power supply or external power pack
- All interface signals & power available on 50 pin ribbon cable
- Mountable in NEMA enclosures
- 19" rack mount panel available, model RMT-02
- Read back data from output device
- Uses standard PB-16A I/O rack available from many Manufacturers
- Detachable Screw Terminals greatly reduce field wiring and replacement time

APPLICATIONS

- Energy management
- Process control
- Product testing
- Laboratory automation

FUNCTIONAL DESCRIPTION

MetraByte's MSS-16 I/O module rack and MDI-16 digital interface card combine to form a 16 channel I/O module interface system for the METRABUS. The MDI-16 adapter board connects to the METRABUS cable and performs all METRABUS interface functions. The MSS-16 plugs into the MDI-16 and provides for the installation of up to 16 Solid State I/O modules. Either input or output I/O modules may be installed in the MSS-16. A number of different input and output voltages are available including 120/230 VAC inputs and outputs, 0-60 VDC outputs, 10-32 VDC inputs etc.

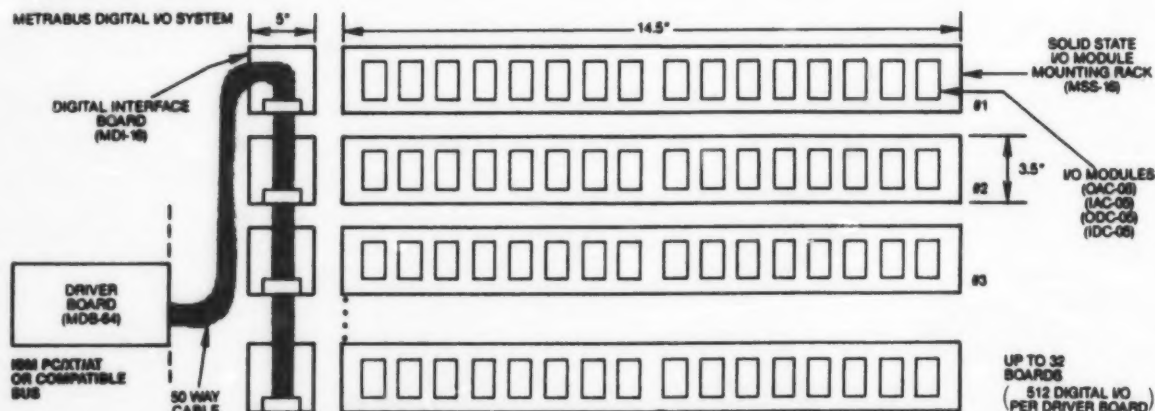
The bank of 16 modules are configured as two 8-bit ports on the METRABUS. Input and Output modules can be mixed within a bank although for simpler programming it is recommended that banks be dedicated to either input or output. Up to 32 racks (512 I/O points) can be controlled by the 64-bit address space of the METRABUS driver card.

The addition of further driver cards allows a single PC to control and monitor thousands of I/O points. Larger systems can be powered from METRABUS power supplies PWR-55 or PWR-100.

The MDI-16 is connected to the METRABUS cable via a 3M 3425-6050 or equivalent connector. The standard METRABUS cable is ten feet long and is designed to connect to 4 METRABUS I/O boards. MetraByte will also build special cables for your application. Screw terminals on the MSS-16 offer easy connection to your application and will accept wire sizes 12-22 awg.

Applications which are to be mounted in 19 inch racks should specify the MDI-16R and not the standard MDI-16. The R signifies a right angle connection to the MSS-16 board. This maintains the maximum length at less than the width of a 19 inch rack. MetraByte's RMT-02 is pre-drilled to accept the MDI-16R and MSS-16. For flat panel (minimum 24 inch width) the in-line MDI-16 and MSS-16 should be used.

BLOCK DIAGRAM



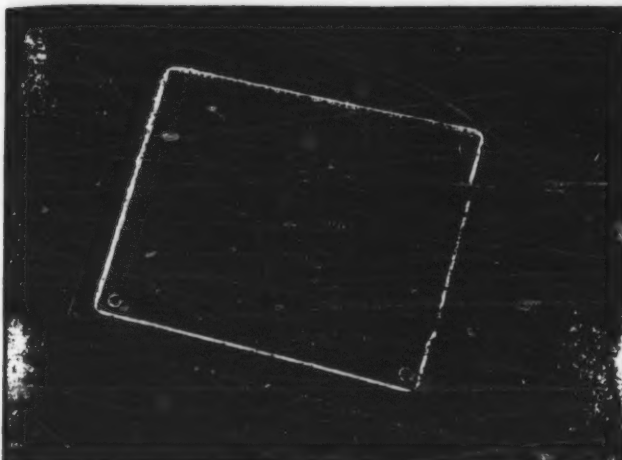


MetraByte
Corporation

**DATA ACQUISITION AND CONTROL
FOR IBM PC/XT/AT AND COMPATIBLE
COMPUTERS**

EXPANSION MULTIPLEXER FOR DAS-20 AND VMECAI-16 BOARDS MODEL EXP-20

65



FEATURES

- Expands any DAS-20 or VMECAI-16 analog input to 16 differential inputs.
- On-board Cold junction temperature sensor for use with thermocouples
- Open channel detection
- Instrumentation amplifier with switch selectable gains of 1, 10, 100, 200, 300, 500, 600, 700 and 800
- Jumper selectable input low pass filter
- Cascadable (up to 16 boards)
- Screw terminals accept 12-22 Awg wire.

APPLICATIONS

- Input expansion
- Input signal conditioning
- Thermocouple measurements
- Energy Management

FUNCTIONAL DESCRIPTION

MetraByte's Model EXP-20 multiplexer offers an extremely inexpensive way to expand the input capabilities of the DAS-20 and VMECAI-16 boards. Each EXP-20 includes 16 fully differential inputs that can be multiplexed into a single A/D board input channel. Daisy chaining additional EXP-20's allows up to 256 analog inputs (16 EXP-20's) to be monitored by a single DAS-20 or VMECAI-16. (256 channel operation is possible only when the A/D board is set for 16 channel single ended operation, only 8 EXP-16's can be connected to a DAS-20 or VMECAI-16 if the board is set in the 8 channel differential mode). The EXP-20 channel to be enabled is determined by a 4 bit digital input (generated by the A/D boards digital output port). An on-board instrumentation amplifier provides 9 switch selectable input gains that range between 1 and 800.

A temperature sensor on the EXP-20 allows the monitoring of the cold junction temperature, and so the EXP-20 is ideally suited to measuring Thermocouple inputs. Cold junction outputs of 20 mV and 200 mV per degree Centigrade are available and selected by a jumper block. Jumpers are also available to connect an open thermocouple detection and a low pass input filter circuit to each EXP-20 input channel. Convenient plated through holes on the board facilitate the installation of shunt resistors for current measurements.

The EXP-20 is mounted in a plastic case when shipped, but may be removed from the case and is easily mounted in 19 inch rack enclosures such as MetraByte's model RMT-02. Screw terminals on the board greatly simplify field wiring and accept wire sizes 12-22 awg.

BLOCK DIAGRAM

